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By

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16. ABSTRACT The report gives results of an advanced test program on a prototype lime/limestone wet-scrubbing test facility for removing SO2 and particulates from coal-fired boiler flue gases. Major effort during the tests was concentrated on evaluating adipic acid as an additive for enhancing SO2 removal efficiency. Results show that adipic acid can substantially improve the performance of limestone spray towers or turbulent contacting absorbers. SO2 removals > 90% and reliable scrubber operation were demonstrated in four long-term (> 1 month) limestone runs. The optimum pH was determined to be about 5.1 with the additive, compared to 5.5-6.0 without. Because of the lower operating pH, limestone utilization was significantly improved, and tests showed lower limestone consumption and reduced waste solids production with the additive. Consequently, both capital and operating costs for an adipic acid enhanced limestone system are estimated to be 5% lower than for a conventional system. The improved limestone utilization also contributes to reliable scrubber operation, thus reducing maintenance costs. Mathematical models were derived which correlate the SO2 removal performance as a function of operating parameters such as gas and slurry flow rate, pH, and adipic acid concentration.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Scrubbers	Pollution Control	13B	13I
Adipic Acid	Calcium Oxides	Stationary Sources	07C	07B
Flue Gases	Calcium Carbonates	Particulate	21B	
Desulfurization	Coal		07A,07D	21D
Dust	Boilers		11G	13A
Aerosols	pH			
Mathematical Models			12A	

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ABSTRACT

This final report presents test results from July 1978 through March 1981 of an Advanced Test Program on a 10-MW equivalent, prototype lime/limestone wet-scrubbing test facility for removing SO_2 and particulates from coal-fired boiler flue gases. Major effort in this period was concentrated on the evaluation of adipic acid, an organic acid buffer, as an additive for enhancing the SO_2 removal efficiency. The test facility was located at Tennessee Valley Authority's Shawnee Steam Plant near Paducah, Kentucky. Tests were conducted on two parallel scrubber systems: a venturi followed by a spray tower or a spray tower alone (35,000 acfm @ 300°F), and a Turbulent Contact Absorber (30,000 acfm @ 300°F).

Test results show that adipic acid is a powerful lime and limestone scrubber additive for improving SO_2 removal. It prevents a large drop in liquor pH at the gas-liquid interface through its pH buffering property, thereby accelerating the liquid-side mass transfer. It also increases the capacity of the bulk liquor for reaction with absorbed SO_2. The optimum concentration of adipic acid is only 700 to 1500 ppm (5 to 10 m-moles/liter) at a scrubber inlet pH of 5.2 or higher.

Because of the lower operating pH allowable for an adipic acid-enhanced limestone system, optimally 5.0 to 5.1 at the scrubber inlet compared to 5.5 to 6.0 usually required for an unenhanced limestone system, the limestone utilization is significantly improved for the adipic acid-enhanced system. This results in reduced limestone consumption and the associated limestone grinding cost, and in a decreased amount of waste solids. Consequently, both capital and operating costs for an adipic acid-enhanced limestone system are approximately 5 percent lower than for a conventional limestone system. The improved limestone utilization also contributes to reliable scrubber operation, thus reducing the maintenance cost associated with the cleaning of an adipic acid-enhanced limestone scrubber.

SO_2 removal efficiencies in excess of 90 percent and reliable scrubber operation have been demonstrated in four long-term (greater than one month) limestone runs with adipic acid enhancement: two venturi/spray tower runs (Runs 907-1A and 907-1B) using two scrubber loops with forced oxidation in the venturi loop, a TCA run (Run 932-2A) without forced oxidation, and a spray tower run (Run 917-1A) with forced oxidation. Full or partial factorial tests, each lasting 12 hours or longer, including 5 to 7 hours of steady-state operation, were also conducted to characterize the SO_2 removal performance of the scrubber as a function of operating parameters such as gas and slurry flow rate, pH, and adipic acid concentration. Data from these tests were correlated using a semi-theoretical mathematical model that conforms to boundary constraints.

Runs of intermediate duration, usually about 5 days, were conducted to define the reliable operating regime and to optimize the levels of operating variables such as pH, air stoichiometry, and adipic acid concentration with respect to adipic acid degradation, calcium sulfite supersaturation, limestone blinding, etc. It was found that adipic acid degradation is minimized when the scrubber is operated at an inlet pH of 5.0 or lower. Forced oxidation increases the rate of adipic acid degradation.

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Section 1

SUMMARY

This is the final report on an Advanced Test Program under the cosponsorship of the Environmental Protection Agency (EPA) and the Department of Energy (DOE)* to test prototype lime and limestone wet-scrubbing systems for the removal of sulfur dioxide (SO_2) and particulate matter from coal-fired boiler flue gas. This report covers the period from July 1978 through March 1981, in which the major effort was on improving the SO_2 removal efficiency by use of adipic acid as an enhancing agent.

The test facility was located at the Tennessee Valley Authority (TVA) Shawnee Steam Plant near Paducah, Kentucky. Bechtel National, Inc. of San Francisco was the major contractor and test program director, and TVA was the constructor and facility operator.

The initial test program at the Shawnee Test Facility began in March 1972. The results of testing from March 1972 through June 1978, in which Bechtel and TVA also served in the same respective roles, are presented elsewhere (References 1 through 6). In this earlier period, major emphasis was placed on solving scaling and plugging problems of the scrubber and mist eliminator, improving the limestone utilization, improving the SO_2 removal efficiency by use of a magnesium oxide additive, and developing forced-oxidation procedures for converting predominantly calcium sulfite sludge to calcium sulfate (gypsum), to improve dewatering and handling characteristics of the waste sludge.

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*The EPA was the original sponsoring agency, but beginning in October 1979 (Fiscal Year 1980) the DOE contributed part or all of the funds for this program.

There were two parallel scrubber trains operated during the reporting period:

- A venturi followed by a spray tower - Train 100
- A Turbulent Contact Absorber (TCA) - Train 200

In June 1980, the venturi scrubber was removed from Train 100, allowing operation with a spray tower-only configuration. Each scrubber train was capable of treating approximately 10-MW equivalent of flue gas (maximum rates of 35,000 acfm* at 300°F for the venturi/spray tower and 30,000 acfm at 300°F for the TCA). The flue gas normally contained 1400 to 3500 ppm SO_2, and could be withdrawn from either the upstream or downstream side of the Boiler No. 10 particulate removal equipment, allowing testing with either high fly ash loading (2 to 7 grains/ dry scf) or low fly ash loading (0.2 to 0.6 grain/dry scf). In addition, the flue gas could also be withdrawn from the upstream side of the Boiler No. 9 particulate removal equipment, allowing uninterrupted testing of either train when Boiler No. 10 was out of service.

The great majority of tests conducted during this reporting period were with adipic acid enhancement of limestone and lime scrubbing systems. Adipic acid is a six-carbon straight-chain dicarboxylic acid, $HOOC(CH_2)_4COOH$. Test results have shown it to be a very powerful additive for enhancing SO_2 removal in conventional limestone or lime scrubbers when present at concentrations of only 700 to 1500 ppm in the scrubbing liquor. It does so by preventing a large drop in pH at the gas-liquid interface through its pH buffering property and thereby increasing the liquid-side mass transfer coefficient.

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*Although it is the policy of the EPA to use the metric system for quantitative descriptions, the British system is used in this report for consistency with previous reports on the Shawnee test results (References 1 through 6). Readers who are more accustomed to metric units are referred to the conversion table in Appendix A.

Most of the tests with adipic acid were conducted on limestone systems with forced oxidation because economic studies have shown that such systems are best suited for most utility flue gas desulfurization (FGD) applications.

An economic study (see Section 24) showed that, for forced oxidation systems designed to achieve an average of 90 percent SO_2 removal from high sulfur flue gas, the capital investments are 4 to 5 percent lower and the operating costs are 5 to 7 percent lower for adipic acid-enhanced limestone systems than for a limestone system without additive. The major savings result from the reduced limestone requirement and the associated grinding operation, and in the reduced quantity of waste solids that need to be disposed of in the adipic acid-enhanced system. The lower limestone requirement is the result of lower operating pH, optimally 5.0 to 5.1, allowable for an adipic acid-enhanced system compared to 5.5 to 6.0 pH usually required for an unenhanced limestone system.

In addition to the economic advantage, adipic acid also offers a number of other attractive features (see Section 3):

- ease in handling
- abundant supply and small required quantity
- ease of retrofit application
- limestone dissolution rate not a controlling factor in the overall reaction rate, allowing the use of a smaller effluent hold tank
- improved scrubber operating reliability due to increased limestone utilization
- lower operating pH, leading to process improvements such as easier forced oxidation, a reduced possibility of calcium sulfite scaling, better automatic pH control in a limestone system, and greater selection of limestone type

- pH buffer mechanism unaffected by forced oxidation or by the presence of chloride in the liquor
- insignificant effect on solids dewatering properties
- insignificant contribution to total dissolved solids

Detailed results of testing on the two scrubber trains are presented in Sections 4 through 22. Table 2-1 presents a summary of the test categories according to alkali type, fly ash loading, adipic acid addition, and forced oxidation scheme. The important characteristics of adipic acid as a scrubber additive and the major conclusions obtained from these tests are summarized below:

- Adipic acid significantly improves the SO_2 removal efficiency.
- The effective scrubber inlet pH is only about 5.2. The buffer capacity of adipic acid is fully utilized at a scrubber inlet pH of 5.2 or higher.
- At a scrubber inlet pH of 5.2 or higher, the optimum concentration of adipic acid is only 700 to 1500 ppm.
- Scrubber inlet pH lower than 5.2 can be used provided it is sufficiently high to allow some ionization of adipic acid. However, higher adipic acid concentration would be required to compensate for the reduced buffer capacity per mole of adipic acid.
- At pH levels lower than 5.2, limestone utilization is usually greater than 85 percent for an adipic acid-enhanced limestone system, as compared to 65-70 percent at higher pH needed for an unenhanced limestone system to achieve an equivalent SO_2 removal.* The increased limestone utilization improves the scrubber operating reliability, reduces the limestone consumption, reduces the quantity of waste sludge, and improves the overall economy.
- With proper pH control and sufficient adipic acid concentration (sufficient buffer capacity in the liquor), steady outlet SO_2 concentrations can be maintained even with wide fluctuations in inlet SO_2 concentration.
- Unlike an unenhanced limestone scrubber, the rate of limestone dissolution is not a rate-controlling step in SO_2 absorption for an adipic acid-enhanced limestone system. Therefore, adipic acid should promote use of less expensive and less energy-intensive limestone rather than lime.

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*Except for the Widows Creek simulation tests (see Section 6), all limestone tests made in this reporting period used Fredonia, Kentucky, limestone having a ground size of about 91 percent less than 325 mesh (Appendix C).

- The mechanism by which adipic acid enhances SO_2 removal is not affected by forced oxidation or by the presence of chloride in the liquor. Thus, it is especially attractive for very tightly closed liquor loop operation such as that achievable with forced oxidation and with a filter as the final solids dewatering device.

- When adipic acid is used in a lime system, both good SO_2 removal and sulfite oxidation can be achieved in a one-loop scrubbing system using within-loop forced oxidation. In this operating mode, calcium adipate becomes the major SO_2 scrubbing species.

- Within-scrubber-loop forced oxidation increases the SO_2 removal efficiency, with or without adipic acid addition, when the SO_2 removal is not dependent on the sulfite-bisulfite buffer.

- The slurry filtration properties are not adversely affected by the presence of adipic acid. Only the initial settling rate of oxidized limestone slurry is somewhat reduced.

- Adipic acid degradation and other unaccounted losses required a feed rate up to 5 times the rate the adipic acid leaves the scrubber system in the liquid phase of the discharged sludge. However, the consumption over the ranges anticipated has negligible economic impact.

- Some decomposition products of adipic acid, such as valeric acid, have a noticeable odor. However, this has not been a problem in testing to date.

- Both high pH and forced oxidation contribute to higher adipic acid degradation. Without forced oxidation, essentially no degradation occurs at a scrubber inlet pH below about 5.0.

- Operating a scrubber at low pH and high adipic acid concentration can actually result in lower adipic acid consumption than operating at a high pH and low concentration for the same SO_2 removal.

- The optimum scrubber inlet pH for an adipic acid-enhanced limestone scrubber appears to be 5.0 to 5.1 with respect to adipic acid consumption, limestone utilization, calcium sulfite scaling potential, and the sensitivity of SO_2 removal to variations in pH and inlet SO_2 concentration.

- Results from Level 1 bioassay analysis show that there are no measurable differences in toxicity or mutagenicity between flue gas and slurry samples from limestone scrubbers operating with and without adipic acid.

In addition to the above findings, reliable scrubber operation and SO_2 removal in excess of 90 percent have been demonstrated in the following long-term (greater than one month) limestone runs with adipic acid:

- Two two-scrubber-loop venturi/spray tower runs with forced oxidation in the venturi slurry loop (Runs 907-1A and 907-1B, see Section 4):

  Total onstream hours--2385
  Onstream factor--98.9 percent
  Average SO_2 removal--97 percent
  Sulfite oxidation--98 percent
  Limestone utilization--89 percent
  Filter cake solids content--86 percent
  Adipic acid consumption--8.3 lb/ton limestone
  Adipic acid concentration--1540 ppm in the spray tower
  2260 ppm in the venturi
  Scrubber inlet pH--5.40 in the spray tower
  4.65 in the venturi

- One one-scrubber-loop TCA run without forced oxidation (Run 932-2A, see Section 13):

  Onstream hours--833
  Onstream factor--99.0 percent
  Average SO_2 removal--96 percent
  Sulfite oxidation--21 percent
  Limestone utilization--82 percent
  Centrifuge cake solids content--61 percent
  Adipic acid consumption--9.2 lb/ton limestone
  Adipic acid concentration--1620 ppm
  Scrubber inlet pH--5.30

- One one-scrubber-loop spray tower run with two-tank forced oxidation (Run 917-1A, see Section 12):

  Onstream hours--1688
  Onstream factor--95.6 percent
  Average SO_2 removal--93.4 percent
  Sulfite oxidation--99.8 percent
  Limestone utilizaiton--92.6 percent
  Filter cake solids content--86 percent
  Adipic acid consumption--5.4 lb/ton limestone
  Average adipic acid concentration--1550 ppm
  Scrubber inlet pH--5.05

Full or partial factorial tests have also been conducted on the two scrubber trains. These tests have been correlated successfully using a semi-theoretical mathematical model of the form (see Section 22):

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp\left\{-\alpha_1 L^{\alpha_2}(1/v)^{\alpha_3}\exp\left[\alpha_4 h_s+\alpha_5 pH_i+\alpha_6 A\right]\right\} \qquad (1\text{-}1)$$

where:

L = slurry flow rate per unit scrubber cross-sectional area, gpm/ft^2
v = scrubber gas velocity, ft/sec
h_s = total static height of spheres (for TCA only), inches
pH_i = scrubber inlet liquor pH
A = adipic acid concentration in liquor, ppm
α_1-α_6 = positive constants fitted to the data

The equation is compatible with boundary constraints on SO_2 removal and operating variables (e.g., SO_2 removal as predicted by the equation varies between zero and 100 percent, and zero removal at zero slurry flow rate) and permits reasonable extrapolations beyond the range of fitted data. This form of equation usually explains better than 90 percent of the variation in the data for SO_2 removal, with a standard error of estimate of 2 to 4 percent SO_2 removal.

Limestone blinding by calcium sulfite, as evidenced by the low limestone utilization and/or low pH, has been encountered during limestone tests both with and without adipic acid-enhancement. This phenomenon occurs when the slurry is depleted of solid calcium sulfite crystals, which results from either forced oxidation or high natural oxidation. Under this condition, calcium sulfite in the liquor preferentially precipitates on, and blinds, the alkaline limestone particles. In most cases, increasing the rate of oxidizing air to impart a more vigorous oxidation intensity in the liquid phase would eliminate the limestone blinding. The higher oxidation intensity essentially forces the liquid phase to become unsaturated with respect to calcium sulfite, thus preventing its precipitation. Section 25 describes in detail the system behavior during limestone blinding, the conditions leading to it, and the recommended solutions for eliminating or avoiding limestone blinding.

The results of the routine particulate measurement tests (see Section 27) showed that neither scrubber train could meet the particulate emission standard of 0.03

lb/10^6 Btu when operating with flue gas having high fly ash loadings of 2 to 7 grains/dry scf. On very few occasions the standard was met when the TCA was operated with low fly ash loading of 0.2 to 0.6 grains/dry scf.

Operating experience with the equipment during the reporting period is summarized in Section 31, which also presents the results of corrosion and erosion studies of various materials by TVA.

Section 2

INTRODUCTION

In June 1968 a program was initiated under the direction of the Environmental Protection Agency (EPA)* to test prototype lime and limestone wet-scrubbing systems for removing SO_2 and particulates from flue gases. A test facility was built which operates with flue gas from coal-fired Boiler No. 10 at the Tennessee Valley Authority (TVA) Shawnee Steam Plant, Paducah, Kentucky. Bechtel Corporation of San Francisco was the major contractor and test director, and TVA was the constructor and facility operator.

The original testing program at the facility began in March 1972 and lasted until October 1974. Results for this test period are presented in Reference 1. During this original program, emphasis was placed on solving scaling and plugging problems in the scrubber and mist eliminator for the demonstration of reliable operation.

In June 1974 the EPA, through its Office of Research and Development and Control Systems Laboratory, initiated an Advanced Test Program at the Shawnee Test Facility. Bechtel continued as the major contractor and test director, and TVA as the constructor and facility operator. During the Advanced Test program more emphasis was placed on the chemistry of lime and limestone scrubbing. Four progress reports and a final report have been published (References

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*The National Air Pollution Control Administration prior to 1970.

2, 3, 4, 5, and 6) which document the results of the Advanced Test Program from October 1974 through June 1978.

Major achievements during the Advanced Test Program were:

- Demonstration of reliable operation of the mist eliminators and scrubbers through long-term (greater than one month) tests.
- Establishment of the inter-relationships of SO_2 removal efficiency and operating parameters, such as gas and slurry flow rates, pH, limestone utilization, hold tank design and residence time, magnesium additive concentration, etc.
- Development of mathematical models.
- Development of forced-oxidation procedures to convert the predominantly calcium sulfite sludge to calcium sulfate (gypsum). Such oxidized slurry solids have improved dewatering and handling properties.

In July 1978, the EPA began another test program at the Shawnee Test Facility to further advance the state-of-the-art of flue gas desulfurization. TVA and Bechtel continued their respective roles in this program until the end of March 1981 when the Department of Energy (DOE) took over the management of the facility from the EPA.*

This latest program, entitled "Advanced Testing and Transfer of Shawnee-Developed Technology to Full-Scale Plants", dealt mostly with the improvement of the SO_2 removal efficiency of limestone and lime scrubbers by use of adipic acid, an organic acid buffer, as a scrubber additive. Significant results of testing using adipic acid from July 1978 through May 1980 have been presented elsewhere (References 7, 8 and 9). This Final Report presents in detail the test results from July 1978 through March 1981, covering a 33-month operating period.

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*Beginning in October 1979 (FY 1980), the DOE contributed part or all of the operating fund for the Shawnee Program. TVA and Bechtel shared the test directorship in January through March 1981.

The advantages of adipic acid as an FGD scrubber additive are delineated in Section 3.

Detailed test results, discussions, and summaries of all tests conducted (excluding factorial tests) are presented in Sections 4 through 12 for the venturi/spray tower system and in Sections 13 through 21 for the Turbulent Contact Absorber System (TCA). Test results summary tables, graphical operating data, and average slurry liquor compositions are given in Appendices E through J.

Results of factorial tests, which usually lasted 12 hours or longer including at least 5 to 7 hours of steady-state operation, are presented in Section 22 along with the mathematical modeling of the data.

A brief summary of the characteristics of adipic acid as a scrubber additive is given in Section 23.

Section 24 presents some economics of an adipic acid-enhanced limestone system as compared to an unenhanced limestone system. It is shown that the addition of adipic acid reduces both the capital and operating costs by 4 to 7 percent.

Section 25 describes the phenomenon of limestone blinding by calcium sulfite which was experienced over the years at Shawnee. The causes of limestone blinding and the means of avoiding or eliminating it are presented in this section.

Routine peripheral programs were conducted in addition to the main testing program. These included monitoring of the slurry dewatering properties by cylinder settling and funnel filtration tests (Section 26), and flue gas characterization for particulate and sulfur trioxide emissions (Section 27). Data from these programs are given in Appendices L and M, respectively.

Section 28 presents a correlation of TCA pressure drop for the 1-7/8 inch diameter, 11.5 gram nitrile foam spheres which were used in the reporting period. Previously, smaller spheres of 1-1/2 inches in diameter had been used.

In Section 29, a modified equation is presented for calculating liquid phase ionic imbalance from analytical data. The equation (Reference 4, Section 12) has been revised to include the effect of pH on sulfite-bisulfite equilibrium, the adipate species, and hard-to-oxidize sulfur species (such as dithionate).

Section 30 presents the chemical analysis of various limestones received at Shawnee for a Limestone Type and Grind Program.

Finally, the operating experience with the Shawnee equipment and materials is summarized in Section 31. Conclusions are given wherever possible.

Other relevant information is presented in the following subsections.

2.1 BACKGROUND OF ADIPIC ACID TESTING

As the emission standards for sulfur dioxide become increasingly stringent and the fossil-fueled utilities become hard-pressed to meet these standards, there is a strong incentive to improve the FGD system performance while minimizing the operating costs.

A primary objective of the EPA alkali wet scrubbing test program during the last several years has been to enhance SO_2 removal and improve the reliability and economics of lime and limestone wet scrubbing systems by use of adipic acid as a chemical additive.

Adipic acid is a six-carbon dicarboxylic organic acid, $HOOC(CH_2)_4COOH$, that buffers the pH in the scrubber slurry. In theory, any acid, which is intermediate in strength between carbonic acid and sulfurous acid and whose calcium salt is reasonably soluble, may be employed. However, adipic acid was selected because it is one of the most cost effective organic acid buffers on a molar basis and is commercially abundant. Its main use is as a raw material in the manufacturing of nylon. It is also used as a food additive.

The initial testing of adipic acid by the EPA began in October 1977 in a 0.1-MW in-house pilot plant located at Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), North Carolina (Reference 10). The tests were undertaken as a result of theoretical analyses by Rochelle (Reference 11). Adipic acid effectively buffers the pH in limestone/lime SO_2 absorbers and improves the SO_2 removal efficiency. The buffering action limits the drop in pH at the gas/liquid interface during SO_2 absorption, and the resultant higher concentration of SO_2 at the interface accelerates the liquid-phase mass transfer. The capacity of the bulk liquor for reaction with SO_2 is also increased by the presence of calcium adipate in solution. Thus, the SO_2 absorption becomes less dependent on the dissolution rate of limestone or $CaSO_3$ in the absorber to provide the necessary alkalinity. In the case of limestone scrubbing, it follows that a given SO_2 removal efficiency can be achieved at a lower limestone stoichiometry.

Further analysis by Rochelle (Reference 12) suggested that use of additives would be most attractive economically when used in scrubbers employing forced oxidation. If no decomposition or volatilization of the additive occurs, the makeup requirements of the additive would be minimized by the more tightly closed liquor loop achievable due to the better dewatering properties of the oxidized sludge.

The results from the IERL-RTP pilot plant demonstrated, as predicted by Rochelle, that adipic acid was indeed an attractive and powerful SO_2 removal enhancing agent.

Based on the findings at the IERL-RTP pilot plant, a program was set up at the 10-MW Shawnee Test Facility with a major objective of developing commercially usable design data for adipic acid as a chemical additive. Actual testing at Shawnee began in July 1978, and lasted through March 1981, a period of 33 months.

2.2 TEST FACILITY

Initially the Shawnee Test Facility included three parallel lime/limestone wet scrubbing systems, all operating on flue gas from Boiler No. 10 at the Shawnee Steam Plant. However, one system (Train 300, Marble-Bed absorber) was discontinued in July 1973 because of operational difficulties. The two scrubbers in operation during the reporting period were:

- A venturi followed by a spray tower (Train 100)
- A Turbulent Contact Absorber, or TCA (Train 200)

These scrubbers were chosen for their ability to remove both SO_2 and particulates from the burning of medium- to high-sulfur coal. Each system has a capacity for treating approximately 10 MW equivalent of flue gas (35,000 acfm @ 300°F for the venturi/spray tower and 30,000 acfm @ 300^{o}F for the TCA).

The venturi was manufactured by Chemical Construction Co. and contains an adjustable plug that permits control of pressure drop over a wide range of flow conditions. The spray tower is a round vessel and contains four spray headers spaced 4 ft apart. The bottom header (Header No. 1) sprays the slurry either upward or downward. The three upper headers (No. 2, 3, and 4) discharge the slurry downward. The spray tower proper and the mist eliminator section are both 50 ft^2 in cross-sectional area.

The TCA was manufactured by Universal Oil Products. It is a square vessel with 32 ft^2 of cross-sectional area, and contains three beds of mobile spheres which are retained by four bar grids spaced approximately 4 ft apart. The mist eliminator is housed in an expanded section having 49 ft^2 (7 ft x 7 ft) in cross-sectional area.

Each system has its own slurry handling and dewatering facilities. The flue gas, which normally contains 1400 to 3500 ppm by volume of SO_2, is obtained either upstream (containing high fly ash loading of 2 to 7 grains/dry scf) or downstream (containing low fly ash loading of 0.2 to 0.6 grain/dry scf) from Boiler No. 10 particulate removal equipment. In addition, the flue gas can also be withdrawn from the upstream side of the Boiler No. 9 particulate removal equipment, allowing uninterrupted testing of either train when Boiler No. 10 is out of service.

In June 1980, the venturi scrubber was removed from Train 100, allowing operation with the spray tower only. Previous to the removal of the venturi scrubber, operation with a true spray tower-only configuration was not possible without some interference from the venturi, even with its adjustable plug wide-open and minimum slurry flow for flue gas cooling.

2.3 TEST PROGRAM OBJECTIVES AND SCHEDULE

Tests conducted at the Shawnee Test Facility can be classified into test blocks according to the type of alkali, fly ash loading in the flue gas, adipic acid addition, and forced oxidation scheme. Table 2-1 lists the combinations of

TABLE 2-1

TEST BLOCKS CONDUCTED AT SHAWNEE

Test Block	Alkali	Fly Ash Loading	Adipic Acid Addition	Oxidation Scheme	No. of Tanks in Oxid. Loop
Venturi/Spray Tower System:					
1	Lime	High	Yes	2-Loop	2
2	Lime	High	Yes	No	-
3[a]	Limestone	High	Yes	2-Loop	2
4	Limestone	High	Yes	2-Loop	1
5	Limestone	High	Yes	1-Loop	2
6	Limestone	High	Yes	1-Loop	1
7	Limestone	High	Yes	Bleed Stream	-
8	Limestone	High	Yes	No	-
9[b]	Limestone	High	No	2-Loop	2
Spray Tower System:					
10[a]	Limestone	High	Yes	1-Loop	2
11	Limestone	High	Yes	No	-
12	Limestone	High	No	1-Loop	2
13	Limestone	High	No	No	-
TCA System:					
14	Lime	High	Yes	1-Loop	1
15	Lime	High	Yes	No	-
16[a]	Lime	High	No	No	-
17	Limestone	High	Yes	1-Loop	2
18	Limestone	High	Yes	1-Loop	1
19[a]	Limestone	High	Yes	No	-
20	Limestone	High	No	1-Loop	1
21[c]	Limestone	High	No	No	-
22[d]	Limestone	Low	Yes	1-Loop	1
23[d]	Limestone	Low	Yes	No	-

[a] Includes long-term (greater than one month) tests

[b] Widows Creek forced oxidation simulation tests

[c] Glitsch Grid packing tests

[d] Springfield adipic acid simulation tests

these variables which have been tested at Shawnee, including factorial tests. The test schedule is shown in Figure 2-1.

As can be seen, major emphasis during the 33 months of testing was placed on adipic acid-enhanced limestone tests with forced oxidation. Forced oxidation was emphasized since it results in better sludge dewatering properties and reduced waste solids disposal costs. Furthermore, the more tightly closed liquor loop, achievable as a result of forced oxidation, reduces the adipic acid makeup requirements.

The major objectives in these tests were to demonstrate the effectiveness of adipic acid as a limestone or lime scrubber additive for improving the SO_2 removal efficiency and to develop commercially usable design data for full-scale applications.

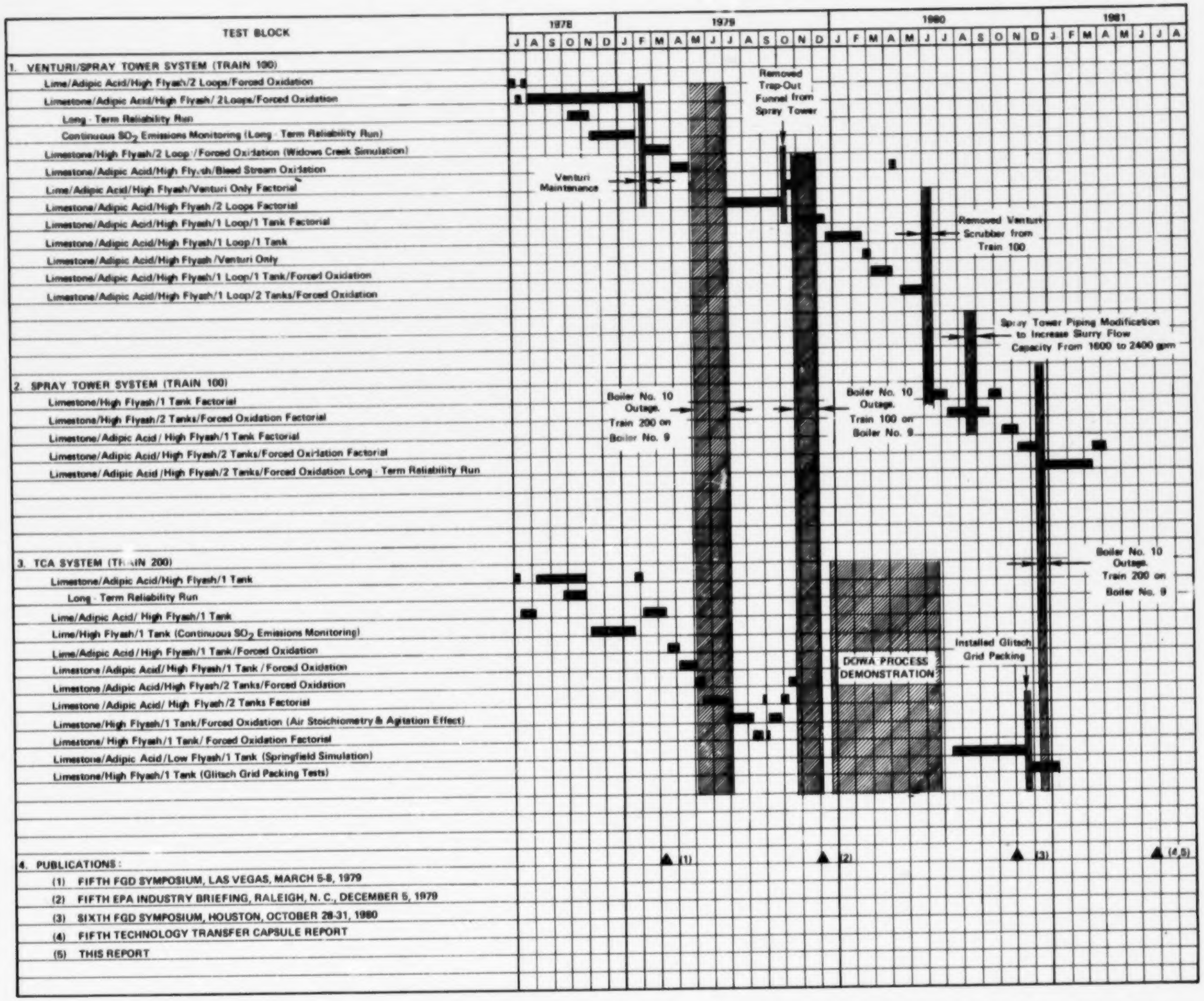
2.4 EPA PILOT PLANT SUPPORT

The 0.1-MW EPA IERL-RTP pilot plant (300 acfm capacity) is capable of simulating the Shawnee scrubber systems with excellent agreement in the lime and limestone wet-scrubbing chemistry.

Preliminary data were generated on the pilot-scale system to determine the validity of new process concepts and to guide the selection of those promising concepts that should logically be investigated on the larger scale Shawnee units. Examples of studies originating at the IERL-RTP pilot plant and then later investigated at the Shawnee Test Facility include gypsum unsaturated operation, increasing limestone utilization, forced oxidation of sulfite to sulfate, and magnesium-enhanced lime and limestone scrubbing. Adipic acid test results from the pilot plant greatly helped the test program planning at the Shawnee Test Facility.

Figure 2-1

Schedule For Advanced Test Program



2.5 ANALYTICAL PROGRAM

To control system parameters and to develop advanced theoretical models by which lime/limestone SO_2 scrubbing systems may be described, routine analyses of scrubber slurry streams were performed. The test facility had a fully staffed and equipped laboratory capable of performing all the required analyses. The type and frequency of these analyses are listed in Table 2-2. A complete description of the analytical procedures used for these analyses can be found in Reference 13.

2.5.1 General Test Schedule

Presented in Table 2-2 is a list of the location and frequency of samples taken and the type of analysis performed on each sample. Basically, the scrubber inlet slurry streams were analyzed for all components every 8 hours. Variables essential to scrubber operation and control were determined more frequently; pH was read every 2 hours, percent solids in the recirculating slurry was determined every 4 hours, and any additive whose concentration was to be controlled was determined every 2 hours.

Scrubber outlet streams were analyzed once every 8 hours for the liquor phase only. This was done to gather data for scrubber characterization. Percent solids in alkali feed, a controlled input, was determined every 2 hours.

Thickener underflow percent solids concentration was determined every 4 hours. The percent solids in the filter and centrifuge cakes was determined every 4 hours to document the dewatering equipment performance and to facilitate material balance calculations.

TABLE 2-2

TYPE AND FREQUENCY OF SAMPLE ANALYSES

Sample Location	Type of Analysis	Frequency of Sampling
Venturi Inlet Spray Tower Inlet TCA Inlet	Complete solids and liquor analysis	Every 8 hours
	Weight percent solids of slurry	Every 4 hours
	pH of slurry	Every 2 hours
	Additive (if any)	Every 2 hours
	Mn or Fe	Every 24 hours
Venturi Outlet Spray Tower Outlet TCA Outlet	Complete liquor analysis	Every 8 hours
Alkali Feed	Weight % solids	Every 2 hours
Clarifier Underflow	Weight % solids	Every 4 hours
Filter	Weight % solids in filtrate	Every 4 hours
	Weight % solids in filter cake	Every 4 hours
Centrifuge	Weight % solids in centrate	Every 4 hours
	Weight % solids in centrifuge cake	Every 4 hours
Special Tests	Buchner Funnel filtration test	Every 24 hours
	Cylinder settling test	Every 24 hours

Special tests were also performed by laboratory personnel. These included a Buchner Funnel filtration test and a cylinder settling test once a day to characterize the slurry solids dewatering properties. The laboratory also conducted special analyses, as needed, on samples such as scrubber scale and solids deposits, recheck samples, etc.

2.5.2 Quality Assurance

The primary method for ensuring reliability of analytical data was the daily evaluation of analytical results by the onsite staff and by Bechtel personnel in San Francisco. Ionic imbalance and the general reasonableness of results were used as the measure of acceptability. Solids analyses with an ionic imbalance greater than ±8.5 percent and liquor analyses with an ionic imbalance (see Section 29) greater than ±15 percent were rejected. The solids ionic imbalance limit of ±8.5 percent was based on the results of about 300 solids analyses performed prior to December 12, 1975. In these analyses, the average ionic imbalance was ±3.5 percent, with a standard deviation of 2.5 percent. Thus, ± 8.5 percent ionic imbalance included approximately 95 percent of the solids analysis results. The liquor ionic imbalance values for 60 analyses performed in July 1976 had an average of ±6.4 percent and a standard deviation of 4.4 percent. Thus, ±15 percent ionic imbalance included 95 percent of the liquor analysis results.

The results of the analysis of liquor and solids standards were used to monitor both the accuracy (closeness between the true and the experimentally determined values) and the precision (reproducibility) of analytical results. Shewhart accuracy control charts were routinely maintained to monitor the results. In addition, a TVA program for interlaboratory comparison of analytical results was initiated. Selected quality assurance samples were routinely sent to the TVA General Analytical Laboratory in Muscle Shoals, Alabama, after their analysis at the Shawnee Test Facility laboratory.

2.6 DATA ACQUISITION AND PROCESSING

Data recorded by onsite personnel were sent to the Bechtel home office in San Francisco where they were analyzed, summarized and plotted on a run-by-run basis.

Onsite, selected raw analytical data for each 8-hour shift were entered into a

National CSS, Inc. (NCSS) computer data file and were verified on a daily basis. San Francisco personnel accessed this data file and loaded it into a NOMAD database on the NCSS system. The database stored the data in a hierarchical order according to scrubber, test run, time, and sample point number. User-written computer programs associated with the database were used to perform further calculations on the raw data, e.g., calculation of percent sulfite oxidation and stoichiometric ratio from solids analytical data. Other user-written programs were used to prepare tables that presented the data for specified times or presented run-averaged data for a specified test sequence. The average, maximum, and minimum values of liquor and solid analyses for all runs (excluding factorial tests) made in the reporting period are presented in Appendix D.

Selected hourly test data and scrubber inspection reports were transmitted daily by telecopier from the test facility to San Francisco. Daily data packages, which provided detailed documentation of each day's operation, were mailed to San Francisco.

Other information such as scrubber operating times and shutdowns were maintained in chart form by the home office personnel and are presented in Appendix B. Data on raw materials such as lime, limestone, coal, and adipic acid are given in Appendix C.

2.7 BECHTEL-MODIFIED EQUILIBRIUM COMPUTER PROGRAM

The liquor equilibrium computer program has been a valuable tool in determining the ionic imbalance of dissolved species and the degree of gypsum saturation from the laboratory-determined pH and species concentrations. The program was originally developed by Radian Corporation and subsequently modified by Bechtel to drastically reduce the converging time of iteration.

The modified program listing, inputs and outputs, and example cases have been presented in Reference 1. Since then, additional modifications to the program have been made to include adipic acid and its ionized species, and to add to the program the capability of handling high concentrations of magnesium. Appendix K presents the latest revision of the equilibrium computer program.

Simplified equations for manually calculating the degree of gypsum saturation of liquor were presented in Reference 6. These equations were fitted to the computer program, and are useful in situations where the computer program could not be readily accessed. In addition, a simplified equation for manually calculating liquid ionic imbalance is presented in Section 29. This equation has been used by the onsite personnel, who did not have ready access to the equilibrium computer program, as a guide to complying with the ±15 percent liquid ionic imbalance criterion mentioned in Section 2.5.2.

2.8 DEFINITION OF TERMS

Terms used in this report are defined below.

2.8.1 Adipic Acid Concentration

Some adipic acid ultimately degrades or decomposes to lower molecular weight (C_1-C_5) paraffinic hydrocarbons. Most of the degraded acid products, e.g., valeric, glutaric, and succinic acids, still offer proper pH buffer range for effective SO_2 removal enhancement.

Since the analytical method employed at the Shawnee laboratory determines total carboxylic acid (see Appendix N), the term "adipic acid concentration" in ppm reported throughout this report refers to "total carboxylic acid expressed as adipic acid".

2.8.2 Closed Liquor Loop

A scrubber system is said to operate with a closed liquor loop when no excess liquor stream is discharged other than that associated with the waste sludge.

Closed loop operation requires either a solids dewatering device (clarifier, filter, centrifuge) or a pond, with recycle of all supernatant liquor to the scrubber system.

For Shawnee closed liquor loop operation, discharge of excess liquor, such as clarifier overflow or filtrate, was not allowed. When a clarifier alone was used, the system waste discharge (clarifier underflow) solids concentration was normally maintained at about 40 percent. With a filter or centrifuge in series with the clarifier, the waste discharge (filter of centrifuge cake) solids concentrations ranged from 50 to over 80 percent, increasing with increased gypsum content. Thus a very "tight" liquor loop was achieved with forced oxidation (high gypsum content in solids) and with filter or centrifuge as a final dewatering device, because the liquor discharged as part of the waste sludge was markedly reduced.

Makeup water (mist eliminator wash, water in fresh alkali addition stream, and pump seal water) was limited to the quantity which left the scrubber system with the flue gas (as evaporated water and entrainment) and discharge sludge (see Section 10, Reference 6).

2.8.3 Air Stoichiometry

For a lime or limestone system using forced oxidation, the air stoichiometry is defined as the number of gram-atoms of oxygen fed to the air sparger per gram-mole of SO_2 absorbed. One mole of sulfite or bisulfite ions ($SO_3^=$, HSO_3^-) requires one atom of oxygen to be oxidized to sulfate or bisulfate ($SO_4^=$, HSO_4^-). The calculated values for air stoichiometry would be higher if the moles of SO_2 oxidized naturally in the scrubber and hold tank are excluded from the moles of SO_2 absorbed.

2.8.4 One-Loop/Two-Loop Forced Oxidation

Forced oxidation was achieved by air sparging of the slurry in an oxidation tank, either on the bleed slurry stream to the solids dewatering system or on the recirculated slurry within the scrubber slurry loop, to convert calcium sulfite solids ($CaSO_3 \cdot 1/2H_2O$) to gypsum ($CaSO_4 \cdot 2H_2O$).

For a one-scrubber-loop forced oxidation system, the slurry effluents from all scrubbers in the system (e.g., the venturi scrubber and spray tower at Shawnee constituted a two-scrubber system, and the spray tower alone or TCA a one-scrubber system) were sent to a single effluent hold tank, which was the oxidation tank.

For a two-loop forced oxidation system, there were two scrubbers (e.g., venturi and spray tower at Shawnee) with effluent from each scrubber going to a separate tank; the effluent hold tank for the upstream scrubber (with respect to gas flow) was the oxidation tank.

For either one-loop or two-loop forced oxidation systems, the oxidation tank may be followed by a second tank in series to provide further limestone dissolution and gypsum desupersaturation prior to recycle to the scrubber.

2.8.5 Gas Velocity

Gas velocity is the velocity of humidified flue gas (125°F wet-bulb temperature) through the scrubber, based upon empty scrubber cross-sectional area (no allowance made for piping, spray nozzles, or other scrubber internals).

Humidification of hot gas (at 300°F) increases the molar gas flow rate by about 7 percent.

The empty cross-sectional areas of the spray tower and TCA were 50 ft^2 and 32 ft^2, respectively.

2.8.6 Liquid-to-Gas Ratio

The liquid-to-gas ratio, or L/G, is the gallons per minute of slurry recirculated to the scrubber divided by the thousands of cubic feet per minute of humidified gas (125°F) flowing through the scrubber. The unit for L/G is expressed as gal/mcf.

2.8.7 Lime/Limestone Stoichiometry and Utilization

Lime/limestone stoichiometry is the molar ratio of the calcium added as lime or limestone to the SO_2 absorbed in the scrubber. Lime/limestone utilization, expressed in percent, is the inverse of stoichiometry, multiplied by 100 percent. The values of stoichiometry and utilization were determined by the analysis of slurry solids.

2.8.8 SO_2 Make-per-Pass

The SO_2 make-per-pass is defined as the number of milligram-moles of SO_2 absorbed in the scrubber per liter of liquor as the recirculated slurry makes one pass through the scrubber.

2.8.9 Particulate Mass Loading

The particulate mass loading of the scrubber inlet or outlet gas is usually expressed as the total weight of solid particles (fly ash and solid reaction products) in grains per dry standard cubic foot of gas (60°F). Particulate emissions standards are usually specified in pounds of particulates in the stack gas per million Btu of boiler heat input. For a typical Shawnee coal and 30 percent total excess air (boiler excess air plus air in-leakage to system), an emission of 0.10 lb particulates/10^6 Btu is equivalent to a stack gas particulate mass loading of 0.052 gr/dry scf.

2.8.10 Statistical Parameters Used with Correlations

The accuracy of correlations of Shawnee data is usually expressed in terms of two statistical parameters: the standard error of estimate and the percent of variation in the data explained (sometimes called the index of determination).

The fraction of variation explained by a correlation is equal to R^2, where R is the correlation coefficient. The equation defining R^2 is:

$$\text{Fraction of Variation Explained} = R^2 = 1 - \frac{\sum(y-y')^2}{\sum(y-\bar{y})^2}$$

where:

y = value of the independent variable for a particular data point

y' = predicted (correlation) value of the independent variable for the same data point

$\bar{y}$ = arithmetic average of all values of the independent variable in the correlated set of data

The percent of variation is equal to 100 x R^2.

The standard error of estimate is defined by the following equation:

$$\text{Standard Error of Estimate} = \sqrt{\frac{\sum(y-y')^2}{n-k-1}}$$

where:

n = number of data points in the correlated set of data

k = number of dependent variables fitted with coefficients

For a normal distribution of errors, or deviations between the measured and predicted values of the independent variable, about two-thirds of the predicted values should be within plus/minus one standard error of the measured values, and about 95 percent within plus/minus two standard errors.

2.8.11 Gypsum Saturation in Liquor

The fraction gypsum saturation of a limestone/lime wet-scrubbing liquor is defined as:

$$\text{Fraction Gypsum Saturation} = \frac{(Ca^{++})(SO_4^{=})}{K_{sp}}$$

where:

(Ca^{++}), $(SO_4^{=})$ = activities of dissolved Ca^{++} and $SO_4^{=}$ ions, respectively, g-mole/l.

K_{sp} = solubility product of gypsum

= 2.2×10^{-5} (g-mole/l)^2 at 50°C

Percent gypsum saturation is 100 percent times the fraction gypsum saturation. The fraction gypsum saturation of Shawnee scrubbing liquors is calculated by inputting the laboratory liquor analytical data into either the Bechtel-Modified Equilibrium Computer Program (Appendix K) or the simplified equations presented in Reference 6.

2.8.12 Effective and Optimum Scrubber Inlet pH

The effective scrubber inlet pH refers to the minimum pH above which the adipic acid buffer capacity is fully utilized. The optimum scrubber inlet pH is the pH at which the scrubber operation is optimized, considering other factors in addition to the adipic acid buffer capacity utilization.

Adipic acid has two pH buffer points. These buffer points are affected by the chloride concentration (see Section 7). At Shawnee where the chloride concentration is usually on the order of a few thousand parts per million, the corresponding buffer points are about pH 4.0 and 5.0. Therefore, an effective scrubber inlet pH of approximately 5.2 is needed so that most of the adipic acid is in the ionized form and its buffer capacity is more fully utilized.

The optimum scrubber inlet pH for an adipic acid-enhanced lime or limestone system, however, is 5.0 to 5.1. This takes into consideration factors other than buffer capacity utilization, such as adipic acid degradation, limestone utilization, calcium sulfite supersaturation, and the sensitivity of SO_2 removal to pH and inlet SO_2 variations.

Section 3

ADVANTAGES OF ADIPIC ACID AS A SCRUBBER ADDITIVE

A number of attractive features of adipic acid as a scrubber additive are presented in this section. Its advantages over inorganic cation additives such as magnesium ions are also described.

3.1 HANDLING

Adipic acid is non-toxic (it is used as a food additive), non-hygroscopic, and usually comes in powder form (crystalline needles). It is easy to handle and no hazards are encountered in the usual applications other than possible dust explosions which are typical of any organic dust.

At Shawnee, it is routinely dry-fed directly to the effluent hold tank, although it has been added to the fresh limestone slurry makeup tank in some instances.

3.2 BUFFER REACTION MECHANISM

The mechanism by which adipic acid buffers the pH is simple. It reacts with lime or limestone in the effluent hold tank to form calcium adipate. In the absorber, calcium adipate reacts with absorbed SO_2 (H_2SO_3) to form $CaSO_3$ and simultaneously regenerates adipic acid (the buffer reaction). The regenerated adipic acid is returned to the effluent hold tank for further reaction with lime or limestone.

With a sufficiently high concentration of calcium adipate in solution, usually on the order of 10 m-moles/liter to react with the absorbed SO_2, the overall reaction rate is no longer controlled by the dissolution rate of limestone, or the dissolution rate of calcium sulfite in the case of lime scrubbing. Therefore, the limestone dissolution rate is not a limiting factor in sizing the effluent hold tank, allowing the use of a smaller tank.

3.3 RETROFIT

Because of the simple mechanism by which adipic acid enhances SO_2 removal, use of adipic acid in an existing lime or limestone scrubbing system does not require expensive equipment modifications or changes in the process flow configuration. Therefore, it is particularly suited for retrofit applications.

The fact that adipic acid may be added at any point in the slurry circuit provides extra flexibility in locating and installing a simple screw feeder and the associated feed and storage hoppers.

3.4 QUANTITY AND CONCENTRATION

Depending on the operating parameters, the degree of degradation, and the tightness of liquor loop, the quantity of adipic acid required is quite small in relation to the alkali feed. At Shawnee, where a filter was normally used as the final sludge dewatering device, the adipic acid consumption rate was usually less than 10 lb/ton of limestone fed to the system, and sometimes as low as 2 lb/ton of limestone. These values correspond to only 0.6 to 3.0 tons of adipic acid per day for a 500-MW plant.

As an illustration of the small quantity involved, Shawnee's 10-MW plant consumed only a few one-pound coffee cans of adipic acid per hour. Each can contained 1.23 pounds of adipic acid. Manual feeding by the operator with a one-pound coffee can was necessary and expedient at Shawnee because the available screw feeders previously used for MgO addition were over-sized.

Adipic acid has two pH buffer points. These are pH 4.5 and 5.5 in the absence of chloride in liquor, and about 4 and 5 with 5000 to 7000 ppm chloride. To fully utilize the buffer capacity of adipic acid, therefore, the slurry pH should be kept above these values. At Shawnee where the chloride concentration is usually a few thousand ppm, a scrubber inlet slurry pH above about 5.2 is sufficient to keep adipic acid fully active (or ionized). The optimum concentration range of adipic acid at pH above 5.2 is only 700 to 1500 ppm. Higher concentration would be required at lower pH to maintain equivalent buffer capacity in liquid. It should be noted that most of the degradation products of adipic acid, such as valeric, glutaric, and succinic acids, are also effective buffers.

3.5 LIMESTONE UTILIZATION AND OPERATING RELIABILITY

Adipic acid-enhanced limestone (or lime) operation can be carried out at a lower pH than unenhanced limestone (or lime) operation. At the effective pH of about 5.2, the corresponding limestone utilization is normally 85 percent or higher for an adipic acid-enhanced system, as compared to 65-70 percent utilization at the higher pH needed in unenhanced limestone systems to obtain an equivalent SO_2 removal. Thus the quantity of waste solids generated is reduced in an adipic acid-enhanced system. Higher limestone utilization also contributes to more reliable scrubber operation.

3.6 OPERATING pH

With proper pH control and sufficiently high adipic acid concentration (sufficient buffer capacity), the scrubber performance is more stable, and steady outlet SO_2 concentrations can be maintained even with wide fluctuations of inlet SO_2 concentrations.

With the lower operating pH (about 4.6 to 5.4) in an adipic acid-enhanced limestone system, compared to the higher pH (about 5.5 to 5.8) usually needed for an unenhanced limestone system, the system becomes more amenable to other process concepts and improvements. Potential advantages of low pH operation are:

- Reduced adipic acid consumption. Adipic acid degradation has been found to decrease with decreasing pH.
- Easier forced oxidation in the scrubber slurry loop or bleed stream, and less air (and compressor energy) required.
- Essentially complete limestone utilization achievable, with resultant improved scrubber operating reliability.
- Reduced sensitivity to limestone type and grind; fine grinding of limestone is probably not required.
- Lower sulfite scaling potential.
- Better prospects (sensitivity) for automatic pH control in a limestone system.
- Greater flexibility for SO_2 emission control; higher sensitivity of SO_2 removal at lower pH allows raising pH to increase the adipic acid buffer capacity and SO_2 removal when needed.
- Applicability to low-sulfur sub-bituminous and lignite coals containing alkaline ashes which are extractable only at low pH.
- Probable lower cost due to all of the above factors.

3.7 ECONOMICS

Since limestone dissolution is not a rate-controlling step in SO_2 absorption for an adipic acid-enhanced limestone system, adipic acid should promote use of less expensive and less energy-intensive limestone rather than lime.

A study by Borgwardt (Reference 14) indicated that adipic acid, added at a concentration of 1400 ppm to a TCA limestone scrubber, can reduce the absorber electricity demand by 30 percent for 90 percent SO_2 removal at the same limestone stoichiometry as unenhanced operation, due to reduced liquid-to-gas ratio and flue gas pressure drop. The additive is most cost-effective, however, when used to increase the limestone utilization.

Adipic acid-enhanced limestone scrubbing has lower projected capital and operating costs than unenhanced limestone or MgO-enhanced limestone scrubbing. This is primarily due to the reduced limestone consumption at the lower operating pH, the associated grinding cost, and the reduced quantity of waste sludge generated. This is presented in more detail in Section 24.

3.8 FORCED OXIDATION

The mechanism by which adipic acid promotes SO_2 removal is not affected by forced oxidation. Therefore, it can be used with both lime and limestone in systems with or without forced oxidation.

Since forced oxidation converts sulfite to sulfate, it has an adverse effect on SO_2 removal in an unenhanced lime system in which sulfite is a major SO_2 scrubbing species. This is also true in MgO-enhanced lime and limestone systems in which the promotion of SO_2 removal relies on an increased sulfite-bisulfite buffer. When adipic acid is used with lime, calcium adipate becomes a major buffer species and, therefore, both good SO_2 removal and sulfite oxidation can be achieved using within-scrubber-loop forced oxidation.

3.9 CHLORIDE EFFECT

The effectiveness of adipic acid is not affected by chlorides, as is the effectiveness of MgO in an MgO-enhanced process. Tests at the IERL-RTP pilot plant showed that SO_2 removal efficiency obtained with 17,000 ppm chloride in the scrubbing liquor was not significantly different from that obtained without chloride under similar levels of adipic acid concentration. Thus, use of adipic acid is especially attractive for systems with a very tightly closed liquor loop.

3.10 SOLIDS DEWATERING

Adipic acid does not significantly affect the settling and filtration properties of oxidized or unoxidized slurry solids, whereas magnesium does. Section 26 presents the results of routine cylinder settling and funnel filtration tests conducted to monitor the solids dewatering properties.

3.11 TOTAL DISSOLVED SOLIDS

Addition of adipic acid does not significantly increase the total dissolved solids in liquid as does magnesium. High total dissolved solids in liquid entrainment increase particulate emissions and fouling tendencies of equipment downstream of the scrubber.

3.12 OTHER CONSIDERATIONS

Other characteristics of adipic acid, although not necessarily advantageous, are discussed below. The market impact of the projected widespread use of adipic acid in lime/limestone FGD systems is also discussed.

3.12.1 Degradation

Adipic acid degrades to lower molecular weight (C_1 - C_5) paraffinic hydrocarbons. The extent of degradation, and hence the required feed rate, varies depending on the operating conditions such as pH, oxidation, and limestone utilization. At Shawnee, the feed rate of adipic acid is usually less than five times the theoretical requirement, which is the rate it is discharged with the waste sludge. However, most of the degradation products such as valeric, glutaric and succinic acids still offer a proper pH buffer range for effective enhancement of SO_2 removal. Consumption over the ranges anticipated has negligible economic impact.

The mechanism of adipic acid degradation is complex. The EPA has initiated several programs to study the degradation phenomena. Contractors involved include University of Texas at Austin, Radian Corporation, Acurex Corporation, and the Research Triangle Institute. Programs have been set up to investigate the effects on degradation of pH, oxidation, and catalysts such as manganese and iron, to develop analytical procedures, and to identify the degradation products. The programs are continuing.

3.12.2 Odor

During testing with adipic acid at the IERL-RTP pilot plant, the scrubber liquor occasionally had a noticeable odor even though the additive feed did not.

The odor has been identified as that of valeric acid, $CH_3\ (CH_2)_3COOH$, which has a detection threshold of 10 ppb. At Shawnee, this odor was rarely noticed and was not a problem.

3.12.3 Toxicity

Although adipic acid is non-toxic and is used in foods as acidulant to provide clean, tart taste and to serve as a buffering agent for pH control, there have been concerns as to the environmental effects of its decomposition products.

A Level 1 bioassay analysis was conducted by EPA on sludge and flue gas samples from Shawnee. The results of the bioassay showed no significant difference in toxicity or mutagenicity between samples from the venturi/spray tower operating with limestone slurry with adipic acid and forced oxidation (giving higher degradation) and samples from the TCA operating with limestone slurry without adipic acid and without forced oxidation.

3.12.4 Market Impact

As widespread use of adipic acid in lime/limestone FGD systems could occur in the near future, there have been concerns regarding its potential impact on the adipic acid market. A market study conducted by Bechtel in December 1979 (Reference 29) indicated that it will be necessary to add one new adipic acid manufacturing plant of 300 million pounds/year capacity to meet the projected total demand of 2.16 billion pounds/year in 1986, assuming maximum use in FGD systems.

The study also indicated that there should be no immediate concern that the FGD requirement for adipic acid would be greater than the available supply. At the time of the study in 1979, the production capacity in the United States was estimated to be about 1.9 billion pounds/year, while the consumption (without FGD use) was 1.6 billion pounds/year. Thus, it was projected that sufficient manufacturing capacity is already available to supply required amounts of adipic acid for both existing market uses and maximum potential FGD uses through 1982.

The projected adipic acid consumption for 1986 in present applications (no FGD use) was estimated to be near 1.9 billion pounds/year, approaching the present capacity. The maximum FGD use in 1986 was calculated to be about 260 million pounds/year based on the following assumptions:

- A total projected FGD capacity of 100,000 MW in 1986.
- Lime/limestone systems comprise 88 percent of the total FGD capacity.
- Adipic acid is used in high sulfur coal lime/limestone systems only, which comprise 85 percent of total lime/limestone systems.
- A boiler capacity factor of 80 percent.
- An adipic acid addition rate of 0.5 lb/hr/MW (or 3 tons/day for 500 MW capacity) based on Shawnee experience with forced oxidation and closed liquor loop operation using a vacuum filter for solids dewatering.

Therefore, the projected total demand for 1986, including the FGD use, was 2.16 billion pounds/year. With the addition of one new plant of 300 million pounds/year capacity, the total manufacturing capacity will be increased from 1.9 to 2.2 billion pounds/year, which is sufficient to meet the requirement through 1986.

Note that the projected FGD use of 260 million pounds/year in 1986 is probably the maximum that can reasonably occur. Actual usage should be lower for the following reasons:

- Some lime/limestone FGD systems will not use adipic acid, either because sufficient SO_2 removal is achieved without the additive, or because other additives such as MgO are used instead.
- FGD systems other than lime/limestone wet scrubbing, such as spray drying absorption and the dual alkali process, may become more significant.

However, one factor that could increase or decrease adipic acid consumption would be a change in the assumed addition rate in commercial operation due to a difference in liquor loop closure from that at Shawnee. It should be pointed out that the use of adipic acid can only be considered practical in scrubbers that have a tightly closed liquor loop; i.e., that use vacuum filters or centrifuge for solids dewatering.

Waste acids generated in the manufacture of adipic acid or cyclohexanone can probably be used in the lime/limestone FGD systems in lieu of pure adipic acid. These waste acids contain various amounts of organic acids or their sodium salts, such as adipic, hydroxy caproic, caproic, valeric, succinic, glutaric, etc. These acids have a pH buffer range similar to adipic acid and its degraded product acids and can be used to replace pure adipic acid for a substantial cost savings.

Section 4

VENTURI/SPRAY TOWER TWO-SCRUBBER-LOOP FORCED-OXIDATION LIMESTONE/ADIPIC ACID TEST RESULTS

In December 1976, the venturi/spray tower system was converted to a two-scrubber-loop system with forced oxidation accomplished by sparging air into the first scrubber loop (venturi loop) hold tank (see Section 2.8.4 for the definition of two-loop forced oxidation). Testing of this system began in January 1977. Successful demonstration of this mode of scrubbing has been reported for three alkali types: limestone, lime, and limestone with added magnesium oxide (References 5, 15, and 16).

Beginning in July 1978, tests were conducted with added adipic acid in both lime and limestone systems. With adipic acid, SO_2 removal as high as 98 percent was achieved with both alkalis while concurrently oxidizing the product to gypsum. Results of these adipic acid-enhanced, forced-oxidation tests are reported in this section for the limestone system, and in Section 5 for the lime system.

4.1 SYSTEM DESCRIPTION

The venturi/spray tower system was modified for two-loop scrubber operation with forced oxidation as shown in Figure 4-1. To separate the venturi and spray tower scrubber loops, a catch funnel was installed beneath the bottom spray header of the spray tower. To minimize slurry entrainment through the catch funnel, the bottom spray header was turned upward.

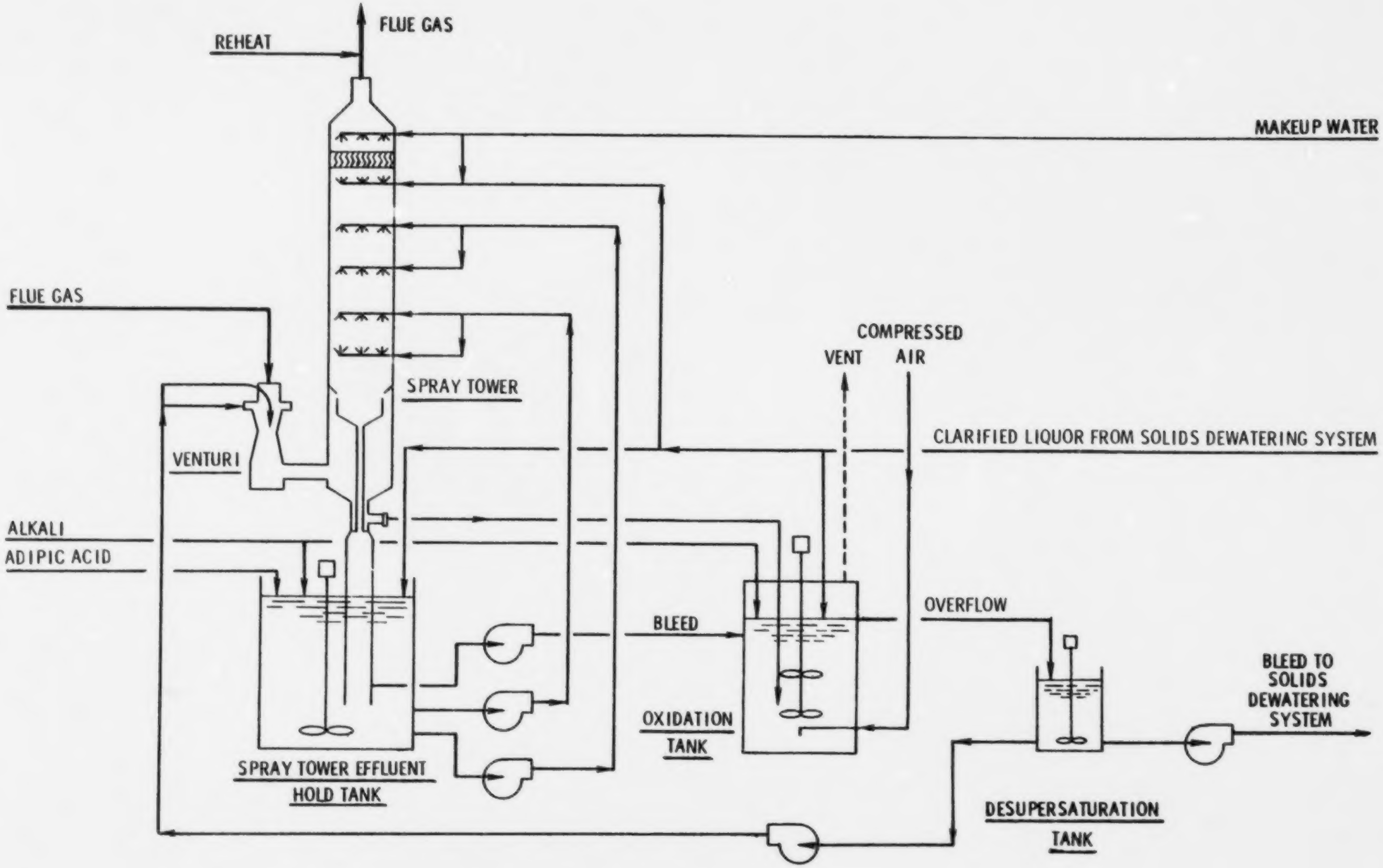

FLUE GAS
REHEAT
MAKEUP WATER
FLUE GAS
SPRAY TOWER
VENTURI
COMPRESSED
VENT
AIR
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
ALKALI
ADIPIC ACID
BLEED
OVERFLOW
OXIDATION TANK
BLEED TO SOLIDS DEWATERING SYSTEM
SPRAY TOWER EFFLUENT HOLD TANK
DESUPERSATURATION TANK

Figure 4-1

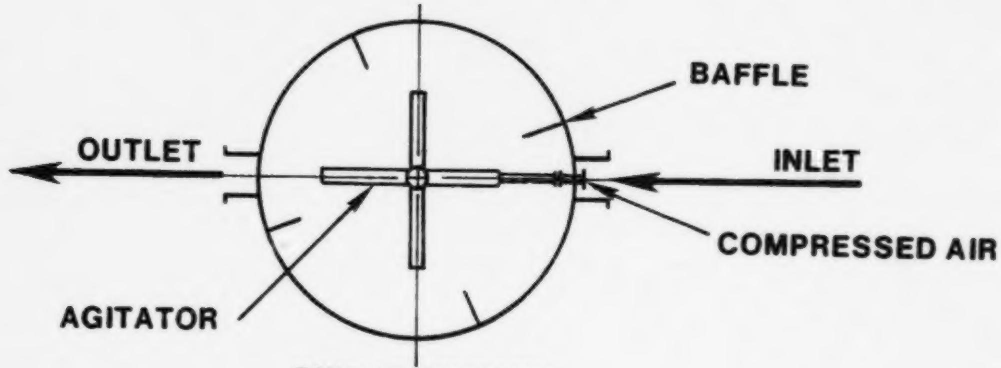
Flow Diagram For Adipic Acid Enhanced Scrubbing In The Venturi/Spray Tower System With Two Scrubber Loops And Forced Oxidation

The hold tank in the first scrubber (venturi) recirculation loop was used as the oxidation tank. The arrangement of this tank is shown in Figure 4-2. The tank was 8 ft in diameter and could be operated at 10, 14, or 18-ft slurry levels. In early tests the tank contained an air sparger ring made of straight 3-inch 316L SS pipe pieces welded into an octagon approximately 4 ft in diameter. It was located 6 inches from the bottom of the tank. Sparger rings had either 130 1/8-inch diameter holes or 40 1/4-inch diameter holes pointing downwards. The sparger ring was fed with compressed air to which sufficient water was added to assure humidification. (Dry air can evaporate water at the sparger orifice and cause scaling). In more recent tests the sparger ring was replaced by a 3-inch diameter pipe with a single open elbow discharging air downward at the center of the tank about 3 inches from the tank bottom. In all tests with adipic acid enhancement, the 3-inch pipe was used for air discharge.

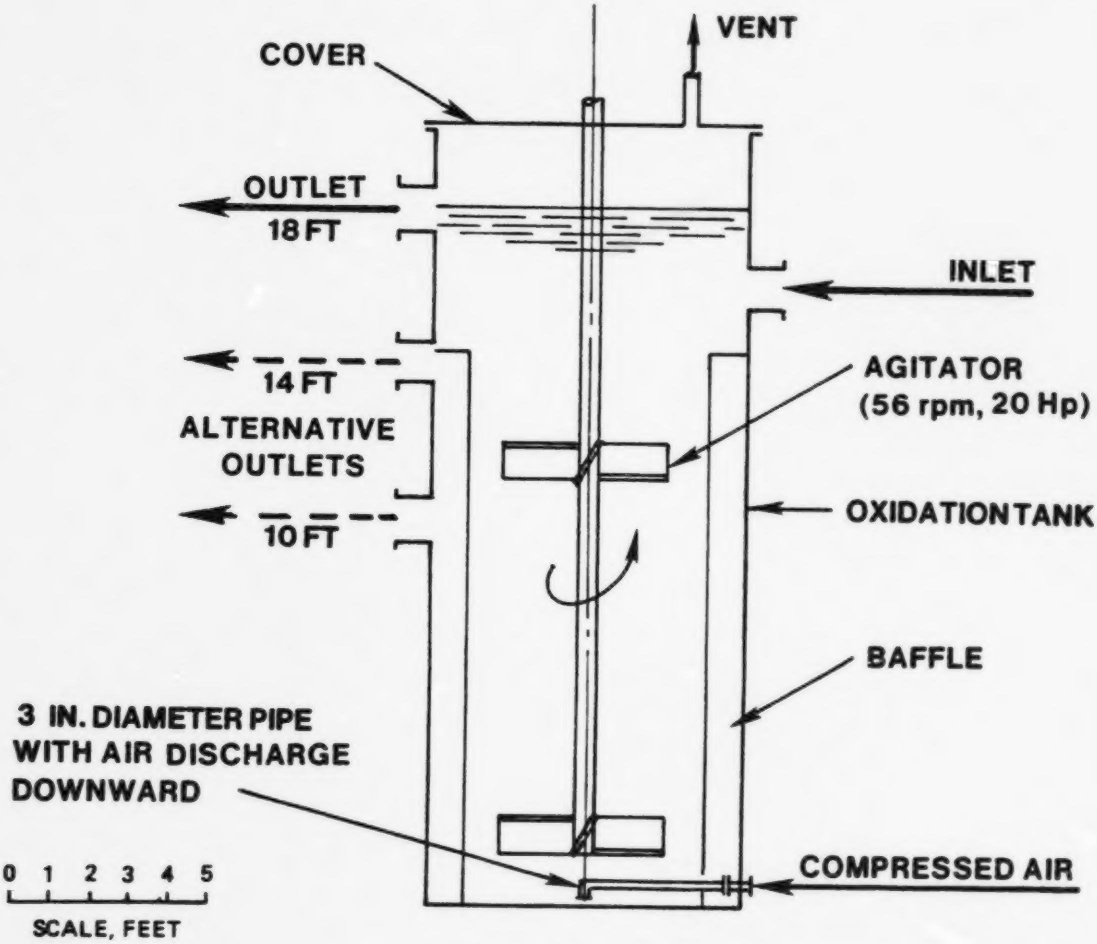
The oxidation tank had an agitator with two axial flow turbines, both pumping downward. Each turbine was 52 inches in diameter and contained 4 blades. The bottom turbine was 10 inches above the air sparger. The agitator rotated at 56 rpm and was rated at 17 brake Hp.

A 10-ft diameter desupersaturation tank, operating at a 5-ft slurry level, followed the oxidation tank to provide time for gypsum precipitation and to provide air-free pump suction.

Provision was made to add alkali to either loop. Adipic acid was added as a dry powder to the spray tower effluent hold tank. The dewatering system consisted of a clarifier followed by a rotary drum vacuum filter. Clarified liquor from the dewatering system could be returned to either scrubber loop or to the mist eliminator wash circuit.


BAFFLE
OUTLET
INLET
COMPRESSED AIR
AGITATOR

OXIDATION TANK
PLAN VIEW


VENT
COVER
OUTLET
18 FT
INLET
14 FT
ALTERNATIVE
OUTLETS
10 FT
AGITATOR
(56 rpm, 20 Hp)
OXIDATION TANK
BAFFLE
3 IN. DIAMETER PIPE
WITH AIR DISCHARGE
DOWNWARD
COMPRESSED AIR
0 1 2 3 4 5
SCALE, FEET

ELEVATION VIEW

Figure 4-2

Arrangement Of The Venturi/Spray Tower Oxidation Tank

4.2 DISCUSSION OF TEST RESULTS

Beginning in July 1978, a series of 10 limestone tests with forced oxidation on the two-loop system was conducted to demonstrate adipic acid as an additive to enhance SO_2 removal. Results of these tests are summarized in Table 4-1. Unless otherwise specified, controlled run conditions common to all of the tests were:

Fly ash loading:	High (2 to 7 grains/dscf)
Flue gas rate:	35,000 acfm at 300°F
Venturi slurry rate:	600 gpm (21 gal/mcf)
Spray tower slurry rate:	1600 gpm (57 gal/mcf)
Venturi slurry solids concentration:	15 percent
Adipic acid in spray tower liquor:	1500 ppm

After operating variables were explored in runs lasting about a week each, SO_2 removals above 95 percent (2400 ppm inlet SO_2 concentration) were achieved in long-term tests at limestone utilizations of about 90 percent and with near complete oxidation.

4.2.1 Effect of Adipic Acid Concentration

The effect of adipic acid on enhancing SO_2 removal can be seen by comparing Run 901-1A (no adipic acid) with Run 902-1A (nominally 1500 ppm adipic acid in the spray tower slurry). Both runs were purposely made at high limestone utilization (97 and 94 percent in Runs 901-1A and 902-1A, respectively) to demonstrate the effect of adipic acid. The addition of adipic acid increased SO_2 removal from 57 percent with no acid to 91 percent at nominally 1500 ppm. These runs were made before conditions for operating with adipic acid were optimized. After optimization, SO_2 removals in excess of 95 percent were routinely achieved at 1500 ppm adipic acid.

Table 4-1

RESULTS OF VENTURI/SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS WITH TWO-LOOP FORCED OXIDATION

Major Test Conditions(1)		901-1A	902-1A	902-1B	903-1A	904-1A	905-1A	906-1A	907-1A(7)	907-1B(7)	908-1A(8)
Fly ash loading		High	High	High	High	High	High	High	High	High	High
Adipic acid concentration in venturi, ppm		0	(~2000)	(~2000)	3500	3500	(~2000)	(~2000)	(~2500)	(2500)	(~2500)
Adipic acid concentration in ST (controlled), ppm		0	1500	1500	-	-	1500(4)	1500	1500	1500	1500
Gas rate, acfm @ 300°F		35,000	35,000	35,000	35,000	18,000	35,000	35,000	18,000-35,000	20,000-35,000	33,000
Venturi slurry rate, gpm		600	600	600	600	600	600	600	600	600	600
ST slurry rate, gpm		1600	1600	1600(2)	0(3)	0(3)	1600	1600	1600	1600	1600
Venturi solids recirculated (controlled), wt.%		15	15	15	15	15	15	15	15	15	15
Residence times (min)/tank level (ft):	Spray tower EHT	14.7/10	14.7/10	14.7/10	-	-	14.7/10	14.7/10	14.7/10	14.7/10	14.7/10
	Oxidation tank	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18
	Desupersaturation tank	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8
Venturi inlet pH (estimate, not controlled)		(~4.5)	(~4.5)	(~4.5)	(~5.5)	(~5.5)	4.5(5)	4.5(5)	4.5(5)	4.5(5)	4.5(5)
Venturi limestone stoichiometric ratio (controlled)		-	-	-	1.3	1.3	-	-	-	-	-
ST limestone stoichiometric ratio (controlled)		1.4	1.4	1.4	-	-	1.45	1.70	1.70	1.70	1.70
Air rate to oxidizer, scfm		210	260	260	210	130	260	260	260	260	260
Run Average Results											
Start-of-Run date		7/12/78	8/3/78	8/22/78	8/28/78	9/5/78	9/8/78	9/27/78	10/8/78	11/13/78	1/29/79
Onstream hours		187	373	65	183	72	439	153	719	1666	119
SO_2 removal, %		57	91	89	53	67	86	93	97.5	97	97
Inlet SO_2 concentration, ppm		2800	2450	2400	2600	2350	2200	2700	2350	2400	2050
Spray tower solids recirculated, wt.%		5.9	4.9	4.8	-	-	3.2	6.8(6)	6.1(6)	6.0(6)	6.8(6)
Venturi inlet pH		4.50	4.45	4.00	4.7	4.75	4.55	4.5	4.65	4.65	4.70
Spray tower inlet pH		5.45	5.25	5.05	-	-	4.75	5.15	5.45	5.35	5.30
Spray tower limestone stoichiometric ratio		1.36	1.65	1.38	-	-	1.53	1.49	1.77	1.78	1.90
Spray tower inlet liquor gypsum saturation, %		95	110	115	-	-	130	100	105	110	105
Spray tower sulfite oxidation, %		28	40	27	-	-	63	28	29	30	40
Overall sulfite oxidation, %		98	98	99	98	98	99	98.5	98.5	98	97
Overall limestone utilization, %		97	94	98	74	76	91	88	88	90	88
Venturi inlet liquor gypsum saturation, %		95	100	90	100	100	100	110	110	105	110
Venturi inlet liquor $SO_3^=$ concentration, ppm		80	55	45	65	60	60	70	65	95	130
Adipic acid concentration in venturi, ppm		0	2045	2355	3510	3690	2315	2495	2360	2160	2220
Adipic acid concentration in ST, ppm		0	1445	1615	-	-	1410	1485	1560	1510	1495
Air stoichiometry, atoms O/mole SO_2 absorbed		2.30	2.05	2.15	2.65	2.80	2.40	1.80	2.0-3.85	1.95-3.45	2.45
Filter cake solids, wt%		85	86	88	83	80	85	84	87	85	86
Mist eliminator restriction, %		0.2	0.2	-	-	0	0	0	0	-	-

Notes:
(1) All runs were made with 9 in. H_2O venturi pressure drop except Runs 907-1A and 907-1B in which pressure drop was 9 in. H_2O at 35,000 acfm.
(2) Intermittent spray tower operation. Spray tower slurry flow turned off 30 minutes every 8 hours. SO_2 removal averaged ~30 percent by venturi only operation.
(3) Venturi alone operation. The spray tower slurry recirculation pumps were turned off for the entire run.
(4) During the initial portion of the run (unsteady state operation) adipic acid was allowed to deplete to observe SO_2 removal/adipic acid relationship.
(5) Venturi inlet pH was controlled by separate limestone addition.
(6) Clarified liquor in excess of mist eliminator wash was returned to spray tower EHT, except for Runs 906-1A, 907-1A, 907-1B and 908-1A where a fraction of this stream was diverted to the oxidation tank to control spray tower slurry solids at 6%.
(7) Long-term reliability test.
(8) Bioassay Sampling Test.

Actual adipic acid concentrations were 1445 ppm in the spray tower loop and 2045 ppm in the venturi loop. Dissolved solids were concentrated in the venturi loop because water was evaporated in humidifying the hot flue gas entering the venturi.

Results at the IERL-RTP pilot plant indicated that most of the enhancement effect with adipic acid may be achieved at concentrations as low as 700 ppm in the slurry liquor. Adipic acid concentrations lower than 1500 ppm were tested later in the reporting period.

4.2.2 SO_2 Removal in the Venturi

Three runs were made to determine SO_2 removal in the venturi alone. In Run 902-1B the spray tower recirculation pumps were turned off for 30 minutes every 8 hours. In Runs 903-1A and 904-1A, only the venturi was operated. All three runs operated at 600 gpm venturi slurry flow rate and a nominal venturi pressure drop of 9 inches H_2O. The results were:

V/ST Run	Flue Gas Rate, acfm	Adipic Acid in Venturi, ppm	Venturi Inlet pH	% SO_2 Removal In Venturi
902-1B	35,000	2355	4.0	30
903-1A	35,000	3510	4.7	53
904-1A	18,000	3690	4.8	67

In Run 902-1B, SO_2 removal was no greater than usually achieved without adipic acid. This was not unexpected because the operating pH was below the 4.0 to 5.0 buffering range of adipic acid.

In Run 903-1A, the pH was increased to 4.7 (limestone stoichiometric ratio of 1.35 mole Ca/mole SO_2 removed) and adipic acid concentration was increased to nominally 3500 ppm with a resultant increase in SO_2 removal to 53 percent. Finally in Run 904-1A, the flue gas flow rate was cut in half to double the liquid-to-gas ratio, resulting in a further increase in SO_2 removal to 67 percent. These tests showed that high removal efficiencies cannot be achieved with reasonably low limestone stoichiometry in the venturi alone. These results are consistent with later tests made with the venturi alone without forced oxidation (see Section 9).

4.2.3 System Control

In previous limestone runs without adipic acid, the limestone stoichiometry in the spray tower loop was controlled by adding limestone to the spray tower hold tank. By using a spray tower limestone stoichiometric ratio of about 1.4, there was sufficient residual limestone in the bleed from the spray tower loop to the venturi loop to maintain the venturi inlet slurry liquor pH above 5.0. This was not the case with adipic acid addition. With adipic acid, the venturi inlet pH fluctuated between 4.0 and 4.5 which was too low to achieve good removal.

Beginning with Run 905-1A, limestone was added to both the spray tower and venturi loops in an attempt to raise the venturi inlet pH. The pH could not be raised above 4.9 even with a limestone stoichiometry greater than 2.0 in the venturi. This was possibly the result of limestone blinding by calcium sulfite (see Section 25).

In subsequent runs, the spray tower limestone stoichiometric ratio was increased to 1.7 to maintain a venturi inlet pH of 4.5. This pH was established as the highest pH in which an overall limestone utilization of about 90 percent could be achieved. Occasionally, limestone is still added to the venturi loop if the venturi inlet pH drops much below 4.5.

4.2.4 Effect of Slurry Solids Concentration

In unenhanced limestone systems, slurry liquor pH and, consequently, SO_2 removal are sensitive to slurry solids concentration (i.e., limestone surface area available for dissolution) below 8 percent. Because of increased liquor buffer capacity with adipic acid enhancement, the system should be less sensitive to solids concentration. However, in early runs with adipic acid, the slurry solids concentration was allowed to drop to sensitive levels. In these runs, clarified liquor from the thickener was returned to the spray tower loop which resulted in low solids concentrations in the spray tower slurry in the range of 3 to 5 percent.

Beginning with Run 906-1A, the spray tower solids concentration was controlled at nominally 6 percent by splitting the clarified liquor return between the spray tower and the venturi loops. The spray tower pH and, consequently, SO_2 removal were increased, as can be seen by the following comparison:

V/ST Run	Spray Tower % Solids	Spray Tower Inlet pH	Spray Tower Limestone Stoich.	Inlet SO_2 Conc., ppm	Percent SO_2 Removal
905-1A	3.2	4.75	1.5	2200	86
906-1A	6.8	5.15	1.5	2700	93

Based on an examination of day-to-day operations, with 1500 ppm adipic acid in a limestone slurry, it appears that SO_2 removal increases with spray tower slurry solids concentration up to about 6 weight percent.

4.2.5 Forced Oxidation

Forced oxidation of the scrubber slurry has been shown to occur equally well with or without adipic acid. In fact, adipic acid buffers the slurry liquor at a low pH favorable for forced oxidation. The adipic acid-enhanced runs on the two-loop system were all operated at air stoichiometric ratios in the range of 1.8 to 2.4 atoms oxygen/mole SO_2 absorbed. Near complete oxidation was achieved in all runs and the filter cake solids concentration of the oxidized slurry was consistently high, in the range of 85 percent or better.

4.2.6 Venturi/Spray Tower Demonstration Runs 907-1A and 907-1B

Run 907-1A was a month-long adipic acid-enhanced limestone run with forced oxidation designed to demonstrate operational reliability with respect to scaling and plugging and to demonstrate the SO_2 removal enhancement capability of the adipic acid additive.

This run was controlled at a nominal 1.7 limestone stoichiometric ratio (up from 1.4 in previous runs) and 1500 ppm adipic acid in the spray tower. Spray tower slurry solids concentration was controlled at 6 percent by splitting the clarified liquor return between the spray tower and venturi loops. Venturi inlet slurry liquor pH was nominally 4.5. Occasionally, limestone addition to the venturi loop was required to maintain this pH.

Flue gas flow rate was varied from 18,000 acfm to a maximum of 35,000 acfm (spray tower gas velocity between 4.8 and 9.4 ft/sec) to follow the daily boiler load cycle which normally fluctuated between 100 and 150 MW. The adjustable venturi plug was fixed in a position such that the pressure drop across the venturi was 9 inches H_2O at 35,000 acfm maximum gas rate. Actual pressure drop ranged from 3.0 to 9.6 inches H_2O.

The slurry recirculation rates to the venturi and spray tower were fixed at 600 gpm (L/G = 21 to 42 gal/mcf) and 1600 gpm (L/G = 57 to 111 gal/mcf), respectively. The oxidation tank level was 18 ft and the air flow rate was held constant at 260 scfm.

The run began on October 8, 1978, and terminated November 13, 1978. It ran for 719 onstream hours (30 days) with no unscheduled outages. The scrubber was down once for a scheduled 3-hour inspection and again when the boiler came down for 135 hours to install a new station power transformer.

Average SO_2 removal for the run was 97.5 percent at 2350 ppm average inlet SO_2 concentration. The SO_2 removal stayed within a narrow range of 96 to 99 percent throughout almost the entire run. On October 19 and on October 27, SO_2 removal dropped briefly to less than 90 percent when the pump which supplied the slurry to the top two spray headers was brought off stream for repacking and the spray tower slurry flow rate was cut in half to 800 gpm. At the reduced slurry recirculation rate, SO_2 removal was 82 to 87 percent.

Venturi and spray tower inlet pH averaged 4.65 and 5.45, respectively. Overall limestone utilization was 88 precent and the spray tower limestone utilization was 56 percent, demonstrating the advantage of good limestone utilization in a two-scrubber-loop operation.

Average adipic acid concentrations were 2360 ppm in the venturi loop and 1560 ppm in the spray tower loop.

Sulfite oxidation in the system bleed slurry averaged 98.5 percent with the air stoichiometric ratio varied between 2.0 and 3.85 atoms oxygen/mole SO_2 absorbed. The filter cake solids content was 87 percent.

The mist eliminator was clean during the entire run. Inspections after 207 hours, 603 hours, and 719 hours (at the end of the run) showed that the mist eliminator was completely free of solids deposits. The system was free of plugging and scaling. There was no increase in solids or scale deposits on the scrubber internals during Run 907-1A.

Following Run 907-1A, a second adipic acid-enhanced limestone run with forced oxidation was made during which flue gas monitoring procedures were evaluated by EPA. This run, Run 907-1B, was made under the same conditions as Run 907-1A except that a "typical" daily boiler load cycle was established for the gas flow-rate to follow, rather than the Unit No. 10 Boiler load. The gas rate was changed as follows to simulate a "typical" boiler load cycle:

Time, hours	Gas Rate, acfm @ 300°F
0100	20,000
0500	30,000
0700	35,000
1100	30,000
1700	35,000
2300	30,000

Run 907-1B began on November 13, 1978 and terminated January 29, 1979. It ran for 1666 onstream hours (69 days) with only 27 hours of scrubber related outages. The scrubber was also out of service for 146 hours when Unit 10 came down for replacement of a broken turbine thrust bearing. Scrubber related outages were:

Plugged slurry line	11 hours
Rebuild bleed pump	10 hours
Miscellaneous mechanical	4 hours
Leak in water supply line	2 hours
Total	27 hours

Excluding boiler outages and scheduled inspections, the combined Runs 907-1A and 907-1B operated for a period of over 3 months with an onstream factor of 98.9 percent. No deposits whatsoever were observed in the mist eliminator for the entire 3-month test period. On only one occasion did solids accumulation cause an outage. The cross-over line carrying slurry effluent from the venturi to the oxidation tank plugged with soft solids and had to be cleaned out. Because of problems associated with converting the Shawnee venturi/spray tower system to two-scrubber-loop operation, this cross-over line followed a tortuous path (see Figure 4-1). A properly designed system would not have this problem.

Results of Run 907-1B were as good in every respect as those of Run 907-1A. Average SO_2 removal was 97 percent at 2400 ppm average inlet SO_2. With few exceptions, SO_2 removal remained within a narrow band of 95 to 99 percent. SO_2 removal dropped briefly (typically 30 minutes) below 90 percent five times when one of the two spray tower recirculation pumps was taken out of service for maintenance, effectively cutting the slurry recirculation rate in half.

Overall limestone utilization during this run was 90 percent. Sulfite oxidation averaged 98 percent and the waste sludge filter cake quality was excellent, having a solids content of 85 percent.

SO_2 emissions for Runs 907-1A and 907-1B were calculated based on an assumed coal heating value of 10,500 Btu/lb, on 100 percent sulfur overhead (none in the bottom ash), and on an assumed excess air of 30 percent. This excess air corresponds to about 700 ppm inlet SO_2 per 1.0 weight percent sulfur in coal for the above conditions.

Figures 4-3 and 4-4 show calculated SO_2 emissions for Runs 907-1A and 907-1B, respectively. Average SO_2 emissions for each 24-hour period (midnight-to-midnight) are indicated by horizontal lines on the figures. The average SO_2 emission for the entire 3-month operating period was only 0.20 lb/10^6 Btu. The highest 24-hour average SO_2 emission during Run 907-1A was 0.37 lb/10^6 Btu (October 18) and during Run 907-1B was 0.41 lb/10^6 Btu (January 20).

4.2.7 Adipic Acid Consumption

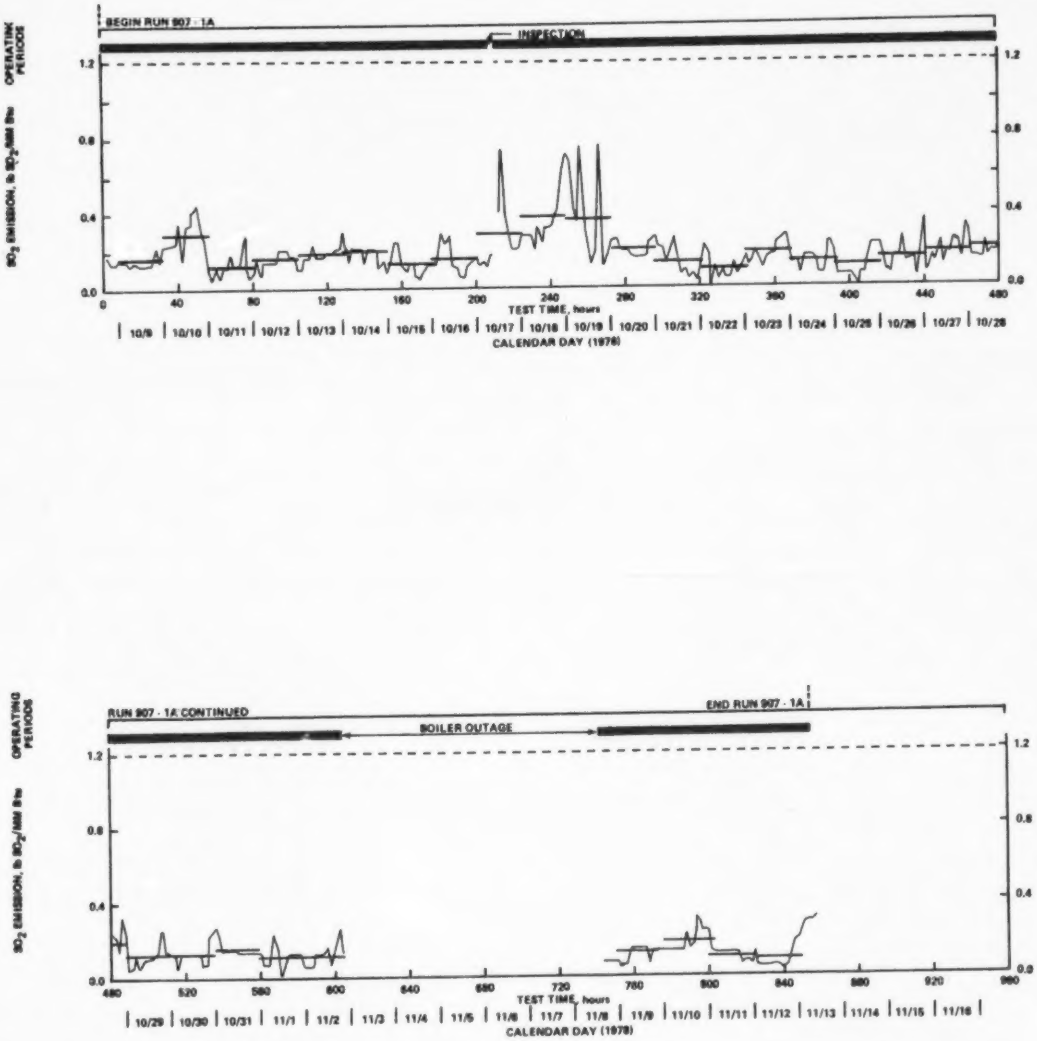
From the onset of testing, adipic acid consumption was higher than anticipated. A material balance calculation for the adipic acid consumption was made for the entire Run 907-1B for a period of 76 days from November 13, 1978, to January 29, 1979. During this period, a breakdown of the average adipic acid addition rate was:

Run 907-1B Adipic Acid Consumption

	lb/hr	lb/ton limestone feed
Discharged with filter cake	0.8	1.8
Unaccounted	2.9	6.5
Total	3.7	8.3

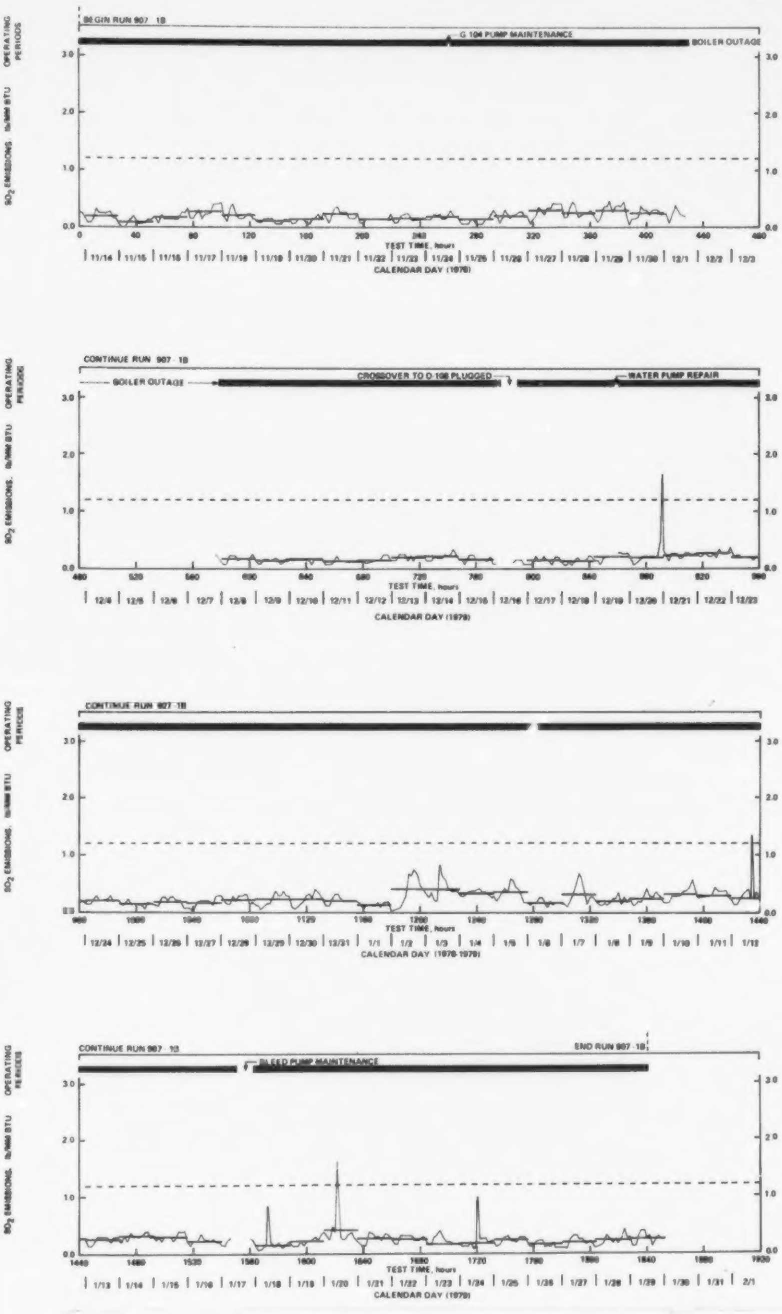
The unaccounted adipic acid loss in this run with forced oxidation was somewhat higher than that recorded in the TCA long-term run, Run 932-2A, without forced oxidation (2.2 lb/hr, see Section 13). Based on this comparision, it appears that forced oxidation in the scrubber system may increase the unaccounted adipic acid losses.

As previously mentioned in Section 3.12.1, EPA has separate programs to investigate these problems. About 600 cubic yards of the gypsum/fly ash mixture from the 3-month combined venturi/spray tower Runs 907-1A and 907-1B were saved in a pile near the test facility. During the winter of 1978-1979, no odor was



Note: Horizontal bars indicate 24-hour (midnight-to-midnight) run averages

Figure 4-3. SO_2 Emissions During Venturi/Spray Tower Run 907-1A



Note: Horizontal bars indicate 24-hour (midnight-to-midnight) run averages

Figure 4-4

SO_2 Emissions During Venturi/Spray Tower Run 907-1B apparent even when the pile was worked by a bulldozer. The results of the evaluation of this pile have been reported elsewhere by the Aerospace Corporation (Reference 17).

4.2.8 Bioassay Sampling Test

Run 908-1A was made under essentially the same conditions as the long-term runs, Runs 907-1A and 907-1B. The run was made to provide flue gas and slurry samples for Litton Bionetics, Inc. and Battelle Columbus Laboratories to conduct Level 1 bioassay analyses under EPA contracts (see Section 3.12.3 of this report and References 18 and 19).

As was expected, the results of Run 908-1A were quite similar to the long-term runs.

4.3 SUMMARY

Although the adipic acid concentration used in this test series was not optimized, reliable operation of the two-loop system was demonstrated in two long-term runs lasting a total of 3 months. SO_2 removal consistently higher than 95 percent and as high as 99 percent was achieved with about 90 percent overall limestone utilization and 1500 ppm adipic acid in the spray tower liquor.

Near complete sulfite oxidation was achieved throughout the tests with resultant filter cake solids concentrations of 84 to 88 percent.

Section 5

VENTURI/SPRAY TOWER TWO-SCRUBBER-LOOP FORCED-OXIDATION LIME/ADIPIC ACID TEST RESULTS

The emphasis at Shawnee has been on adipic acid enhancement with limestone because this combination may prove to be the most economical for achieving high removal in throwaway systems. However, two 10-day runs made on the two-loop venturi/spray tower system in July 1978 demonstrated that adipic acid is also effective in enhancing SO_2 removal in lime systems.

Results of these lime runs are summarized in Table 5-1. The flow configuration and the oxidation tank used for these runs are shown in Figure 4-1 and 4-2, and have been described in Section 4.1.

Run 951-1A was a base case run without adipic acid and Run 952-1A was made under identical conditions with nominally 1500 ppm adipic acid in the spray tower slurry liquor. The addition of adipic acid increased SO_2 removal dramatically from 66 percent with no acid to 98 percent at 1500 ppm (2600 to 2750 ppm average inlet SO_2 concentration).

In these lime runs, all clarified liquor from the dewatering system was returned to the spray tower loop resulting in relatively low spray tower solids concentrations. Apparently, a low solids concentration of 4.5 percent in the adipic acid-enhanced lime run was not detrimental because 98 percent SO_2 removal was achieved. This may be attributed to the high pH inherent in lime

Table 5-1

RESULTS OF VENTURI/SPRAY TOWER LIME/ADIPIC ACID TESTS WITH TWO-LOOP FORCED OXIDATION

Major Test Conditions(1)		951-1A	952-1A
Fly ash loading		High	High
Adipic acid concentration in venturi, ppm		0	(~2000)
Adipic acid concentration in ST (controlled),ppm		0	1500
Gas rate, acfm @ 300°F		35,000	35,000
Venturi slurry rate, gpm		600	600
ST slurry rate, gpm		1600	1600
Venturi solids recirculated (controlled), wt %		15	15
Residence times (min)/tank level (ft):	Spray tower EHT	14.7/10	14.7/10
	Oxidation tank	11.3/18	11.3/18
	Desupersaturation tank	4.7/4.8	4.7/4.8
Venturi inlet pH (controlled)(2)		5.5	5.5
ST inlet pH (controlled)		7.8	7.8
Air rate to oxidizer, scfm		210	260
Run-Average Results			
Start-of-run date		7/3/78	7/20/78
Onstream hours		250	278
SO_2 removal, %		66	98
Inlet SO_2 concentration, ppm		2750	2600
Spray tower solids recirculated, wt %		5.7	4.5
Venturi inlet pH		5.6	5.5
Spray tower inlet pH		7.90	7.75
Spray tower lime stoichiometric ratio		1.14	1.23
Spray tower inlet liquor gypsum saturation, %		90	85
Spray tower sulfite oxidation, %		18	22
Overall sulfite oxidation, %		95	97
Overall lime utilization, %		97	98
Venturi inlet liquor gypsum saturation, %		95	90
Venturi inlet liquor $SO_3^=$ concentration, ppm		130	115
Adipic acid concentration in venturi,ppm		0	1585
Adipic acid concentration in ST, ppm		0	1380
Air stoichiometry, atoms O/mole SO_2 absorbed		2.05	1.80
Filter cake solids, wt %		86	85
Mist eliminator restriction, %		0.5	1

Notes: (1) All runs made with 9 in. H_2O venturi pressure drop. Makeup water and clarified liquor in excess of mist eliminator wash were returned to spray tower EHT.

(2) Venturi inlet pH was controlled by separate lime addition.

systems, at which adipic acid becomes fully effective and calcium adipate is the major scrubbing species. However, in the lime run without adipic acid, the low solids concentration was detrimental. Run 951-1A averaged 66 percent SO_2 removal at 5.7 percent spray tower slurry solids concentration. This run can be compared with a previous one-month lime demonstration run under essentially the same conditions which averaged 88 percent SO_2 removal with 10.4 percent average spray tower slurry solids concentration (see Section 7.2.11, Reference 5). Since sulfite is a major scrubbing species in a lime system without adipic acid, low slurry solids concentration, and hence low calcium sulfite solid dissolution, would have an adverse effect on SO_2 removal.

Section 6

SIMULATION OF TVA WIDOWS CREEK FULL-SCALE FORCED-OXIDATION ON THE VENTURI/SPRAY TOWER SYSTEM

In 1979 TVA conducted a full-scale forced-oxidation demonstration in the scrubber Module D of Boiler No. 8 at their Widows Creek Power Plant in Bridgeport, Alabama. The scrubber system consisted of a venturi followed by a grid tower and operated in a two-scrubber-loop mode using limestone and no adipic acid. Some backmixing of slurry from the venturi loop (oxidation loop) to the grid tower loop was expected by the slurry entrainment in the flue gas.

In order to obtain backup data for the full-scale demonstration, a six-week simulation test program was conducted at Shawnee from mid-February through March 1979 using the venturi/spray tower system with an artificial backmix stream to simulate the full-scale operation. A flow diagram of the set-up at Shawnee is given in Figure 6-1. The details of the oxidation tank are shown in Figure 4-2.

One of the main purposes of the Widows Creek simulation was to test the effect of Widows Creek limestone (Stone Man) and Widows Creek coal (Pittsburgh Midway) on sulfite oxidation, as compared to the oxidation normally observed at Shawnee when Shawnee limestone (Fredonia) and Shawnee coal were used. A wide range of mid- to high-sulfur coals were burned at Shawnee, including Pittsburgh Midway coal. The main concern was that the difference in the catalytic activities, if any, caused by the difference in limestone and coal, might produce a significantly different oxidation efficiency.

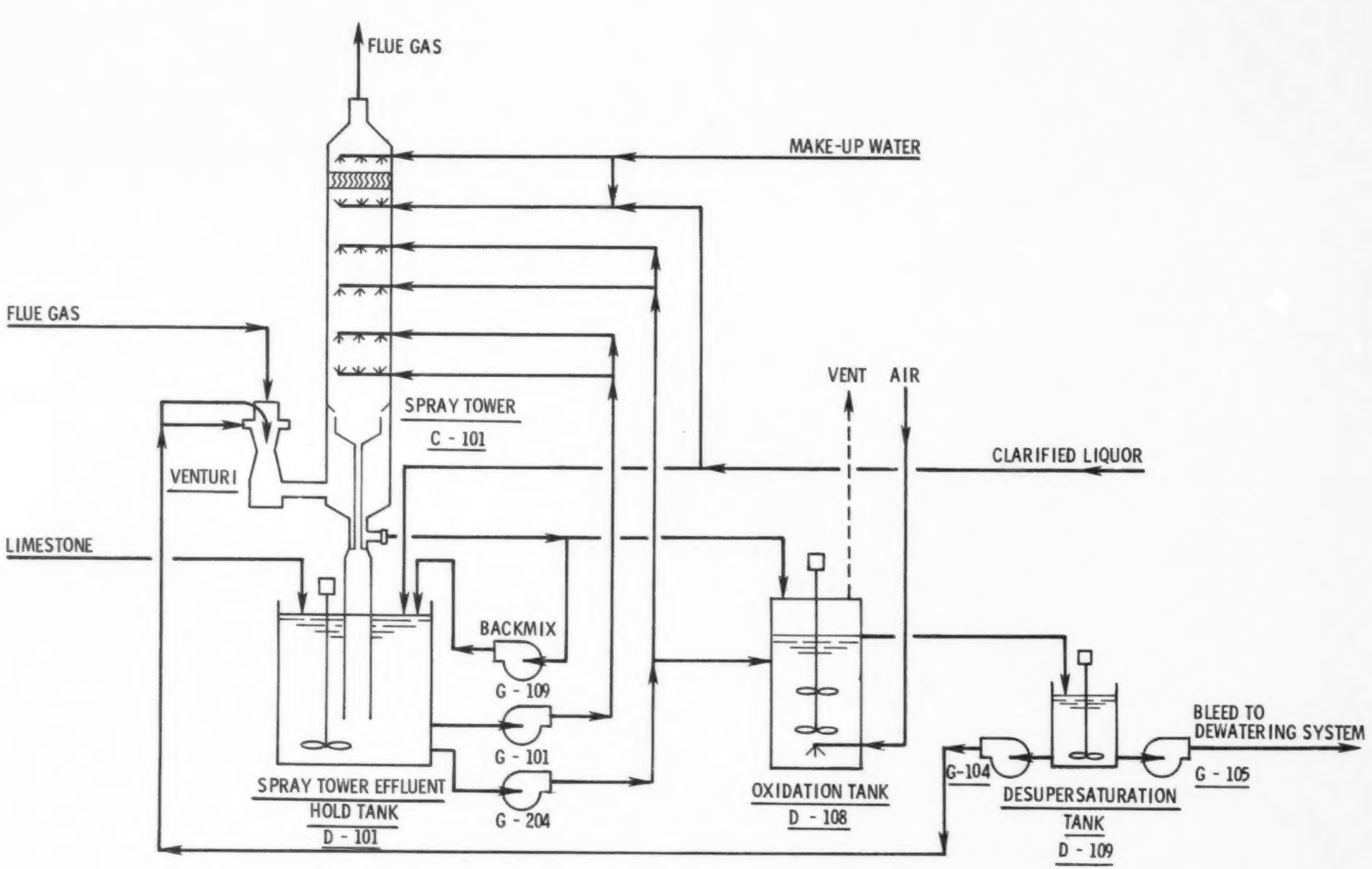

FLUE GAS
MAKE-UP WATER
FLUE GAS
SPRAY TOWER
C - 101
VENT
AIR
CLARIFIED LIQUOR
VENTURI
LIMESTONE
BACKMIX
G - 109
G - 101
G - 204
SPRAY TOWER EFFLUENT
HOLD TANK
D - 101
OXIDATION TANK
D - 108
G-104
DESUPERSATURATION
TANK
D - 109
BLEED TO
DEWATERING SYSTEM
G - 105

Figure 6-1. Flow Configuration For Widows Creek Simulation On The Venturi/Spray Tower With Backmix

Both the laboratory limestone reactivity test results (Reference 5) and the results of this test series indicated that there was a slight difference between Stone Man and Fredonia limestone. All tests showed Stone Man limestone to be somewhat less reactive than Fredonia for SO_2 removal. The particle size distribution of 87 percent less than 325 mesh for Stone Man limestone (ground at Shawnee) was slightly coarser than the typical Fredonia limestone of 91 percent less than 325 mesh used at the test facility.

No difference in sulfite oxidation, with respect to catalytic effect from trace elements, could be detected from the use of Widows Creek coal or limestone. The inlet SO_2 concentrations were very consistent and fell between 2300 and 3100 ppm when Widows Creek coal was used.

6.1 DISCUSSION OF TEST RESULTS

Table 6-1 summarizes the major test conditions and the average results for the 5 runs made in this test series. All runs were made without adipic acid additive.

Run 827-1A. One of the main concerns was that the differences in trace element contents in limestone and coal used at Widows Creek might cause poor or no oxidation of sulfite which has been rather easily achieved at Shawnee. To simulate operating conditions, a portion (65 gpm) of the venturi outlet slurry was returned to the spray tower slurry recirculation system (see Figure 6-1).

A high air stoichiometry was used to assure good oxidation by providing 250 scfm of air to the oxidizer. The resulting air stoichiometry was 2.1 atoms oxygen/mole SO_2 absorbed. Overall oxidation under these conditions was 98 percent with 85 percent solids in the filter cake.

Table 6-1

RESULTS OF VENTURI/SPRAY TOWER LIMESTONE TESTS WITH TWO-SCRUBBER-LOOP FORCED OXIDATION AND BACKMIX -WIDOWS CREEK SIMULATION-

Major Test Conditions[1]	827-1A	828-1A	828-1B	829-1A	830-1A
Fly ash loading	High	High	High	High	High
Gas rate, acfm @ 300°F	35,000	35,000	35,000	35,000	35,000
Venturi liquor rate, gpm	600	600	600	600	600
Spray tower liquor rate, gpm	1500	1500	1500	1500	1500
Venturi percent solids recirculated (controlled)	12	12	12	12	12
Spray tower percent solids recirculated (controlled)[2]	10	10	10	10	10
Residence time (min)/Tank level (ft):					
Spray tower EHT	9.4/6	9.4/6	9.4/6	9.4/6	9.4/6
Oxidation tank	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18
Desupersaturation tank	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8	4.7/4.8
Venturi inlet pH (controlled)	5.5	5.5	(3)	5.5	6.0
Air rate to oxidizer, scfm	250	180	180	145	250
Backmix rate, gpm	65	65	65	65	29
Run-Average Results					
Start-of-Run date	2/14/79	3/12/79	3/13/79	3/16/79	3/22/79
Onstream hours	345	29	48	106	181
Percent SO_2 removal	75	83	59	79	89
Inlet SO2 concentration, ppm	2800	2600	2750	2850	2600
Spray tower percent solids recirculated	10.7	10.6	10.6	10.5	9.9
Venturi inlet pH	5.5	5.55	5.25	5.55	6.0
Spray Tower inlet pH	5.6	5.65	5.0	5.75	6.1
Spray tower limestone stoichiometric ratio	2.0	2.6	2.1	1.7	2.4
Spray tower inlet liquor gypsum saturation, %	100	95	115	90	90
Spray tower sulfite oxidation	72	70	93	65	55
Overall sulfite oxidation, %	98	98	98.5	87	94
Overall limestone utilization, %	60	46	68	70	56
Venturi inlet liquor gypsum saturation, %	100	95	95	95	100
Venturi inlet liquor $SO_3^=$ concentration, ppm	65	115	45	170	85
Air stoichiometry, lb-atoms O/lb mole SO_2 absorbed	2.1	1.45	1.95	1.15	1.90
Filter cake solids, wt%	85	84	84	79	79
Mist eliminator restriction, %	-	-	0	-	0

(1) All runs used Widows Creek limestone (Stone Man) and coal (Pittsburgh Midway). Pressure drop across the venturi was 9 in. H_2O for all runs.

(2) Controlled by splitting the returned clarified liquor to the oxidation tank and spray tower EHT.

(3) Venturi stoichiometry controlled at 1.3.

Table 6-1 shows that the SO_2 removal averaged only 75 percent at an inlet SO_2 level of 2800 ppm. This was lower than what would be expected under conditions of no backmixing, but was not unexpected considering the lower pH of 5.6 in the spray tower inlet slurry caused by backmixing. The closeness of the values in the venturi and spray tower loops indicated that the system approached single loop operation with the backmix.

Run 828-1A. Since good oxidation was achieved in Run 827-1A at a rather high air stoichiometry of 2.1 atoms oxygen/more SO_2 absorbed, air flow rate was reduced to 180 scfm in this run. Sulfite oxidation remained high at 98 percent at an air stoichiometry of 1.45 atoms oxygen/mole SO_2 absorbed.

While oxidation remained high the limestone utilization, which had been low in Run 827-1A (60 percent), became excessively low (46 percent) during Run 828-1A. To achieve better utilization and reduce limestone consumption, a new run was made (Run 828-1B) which operated under limestone stoichiometry control of 1.3 instead of pH control of 5.5 in the venturi inlet slurry.

During Run 828-1A the SO_2 removal increased to 83 percent largely because of a lower SO_2 inlet concentration of 2600 ppm and higher venturi and spray tower limestone stoichiometries.

Run 828-1B. This run was a continuation of Run 828-1A with the limestone stoichiometry in the venturi inlet controlled (at 1.3) rather than the pH. The result was higher limestone utilization (68 percent) but lower pH (5.3 and 5.0 in the venturi and spray tower inlet, respectively) and a subsequently lower SO_2 removal of 59 percent. The lower pH combined with the lower SO_2 removal and the correspondingly higher air stoichiometry of 1.95 assured a good oxidation of 98.5 percent.

Run 829-1A. In this run the control was returned to the venturi inlet pH at 5.5 and the air rate to the oxidizer was further reduced to 145 scfm. The resulting air stoichiometry dropped to 1.15 which in turn reduced overall sulfite oxidation to 87 percent. This confirms earlier tests under standard Shawnee operating conditions which also showed the break point for oxidation (greater than 90 percent) to lie somewhere between 1.1 and 1.5 air stoichiometry.

Despite raising the venturi inlet pH back to 5.5 the overall limestone utilization remained about the same as Run 828-1B at 70 percent. SO_2 removal averaged 79 percent at an average inlet SO_2 concentration of 2850 ppm.

Run 830-1A. In this run the venturi inlet pH was raised to 6.0 to improve the SO_2 removal, the air rate was raised back to 250 scfm (as in Run 827-1A) to insure good oxidation at the higher pH, and the backmix rate was reduced to 29 gpm.

The combination of higher pH and reduced backmix had the predictable effect of raising SO_2 removal to 89 percent at an inlet SO_2 concentration of 2600 ppm. Because of the higher pH (cf. Run 827-1A) sulfite oxidation was only 94 percent. Overall limestone utilization was slightly lower at 56 percent.

Limestone Blinding and $CaSO_3$ Supersaturation. Upon examination of the liquor analytical data, it was found that sulfite concentrations were excessively high for Run 828-1B, averaging 2935 ppm and 2500 ppm at the spray tower inlet and outlet, respectively. For other runs in the test series, sulfite concentrations ranged only from 250 to 700 ppm both at the spray tower inlet and outlet. The apparent $CaSO_3$ supersaturation in the spray tower during Run 828-1B was probably caused by the backmix stream which depleted the $CaSO_3$ solids in the spray tower loop. This was evidenced by the high spray tower solids sulfite oxidation of

93 percent for Run 828-1B, the highest in the test series. $CaSO_3$ must nevertheless crystallize in the spray tower, causing limestone blinding by $CaSO_3$ and the subsequent pH drop in the spray tower (spray tower inlet pH lower than venturi inlet pH in this case) and poor limestone utilization.

6.2 SUMMARY

The following is a summary of the test results:

- No apparent difference in sulfite oxidation could be detected from the use of Widows Creek's Stone Man limestone or Pittsburgh Midway coal. Sulfite oxidation of 98 percent was achieved at 5.5 pH and an air stoichiometry as low as 1.45 atoms oxygen/mole SO_2 absorbed.
- Backmixing of slurry from the venturi loop (oxidation loop) to the spray tower loop depletes $CaSO_3$ solids in the spray tower and could cause $CaSO_3$ supersaturation and limestone blinding in the spray tower.
- Backmixing in effect creates an operating mode approaching that of a single-loop operation.

Section 7

VENTURI/SPRAY TOWER ONE-SCRUBBER-LOOP LIMESTONE/ADIPIC ACID TESTS WITHOUT FORCED-OXIDATION

During factorial tests with adipic acid (see Section 22), when lower scrubber operating pH was explored, it was noticed that the rate of adipic acid addition required to maintain a desired concentration in the scrubber liquor was substantially reduced when the scrubber inlet pH was controlled at 5.0 or lower. At higher pH operation, it is necessary to add adipic acid at up to about 5 times the theoretical addition rate (as defined below), either because of degradation or decomposition of the adipic acid. Apparently, the degradation or decomposition process is inhibited under low pH conditions.

Although the exact mechanism of adipic acid degradation is still not understood, it was decided to investigate the effect of pH on the adipic acid consumption rate in more detail.

Adipic acid has two pH buffer points. At about 1500 ppm adipic acid concentration, the pKa values are about 4.3 and 5.5. These values decrease to 3.9 and 4.9 in the presence of 0.1 g-mole/liter $CaCl_2$ (7000 ppm chloride). Increasing the $CaCl_2$ concentration further to 0.5 g-mole/liter (35,000 ppm chloride) decreases these values only slightly to 3.7 and 4.7 (Reference 20).

Early in the adipic acid-enhanced lime/limestone testing, it was noted that the SO_2 removal enhancement by adipic acid is maximized when the scrubber inlet pH is maintained at about 5.2 or higher under the prevailing scrubber conditions (chloride concentrations). This is because most of the adipic acid is ionized and its buffering capacity more fully utilized at these higher inlet pH levels.

Operations at lower pH therefore require higher adipic acid concentrations to maintain the same degree of SO_2 removal efficiency, because the ionization and buffer capacity of adipic acid are reduced. However, experience at Shawnee shows that the total adipic acid consumption at a scrubber inlet pH below 5.0 and concentration as high as 4000 ppm is actually lower than at a pH of about 5.4 and 1500 ppm when significant degradation was noted.

In addition to reduced adipic acid consumption, lower pH operations also offer several other potential advantages as indicated in Section 3.6. Therefore, low pH operation was emphasized in this and subsequent test blocks.

Seven runs were conducted on the venturi/spray tower system from mid-December 1979 through mid-February 1980 to investigate the effect of pH on the adipic acid consumption rate.

7.1 SYSTEM DESCRIPTION

A single effluent hold tank was used without forced oxidation for Runs 926-1A through 926-1E, 926-1G and 926-1H. The trap-out funnel that had been installed to provide two-scrubber-loop operation (see Figure 4-1) was removed from the spray tower in early October 1979 to allow one-scrubber-loop operation. Figure 7-1 shows the flow configuration used for these tests.

7.2 DISCUSSION OF TEST RESULTS

Table 7-1 summarizes the major test conditions and the run-average results for the seven tests made in this series. The scrubber inlet pH and the adipic acid

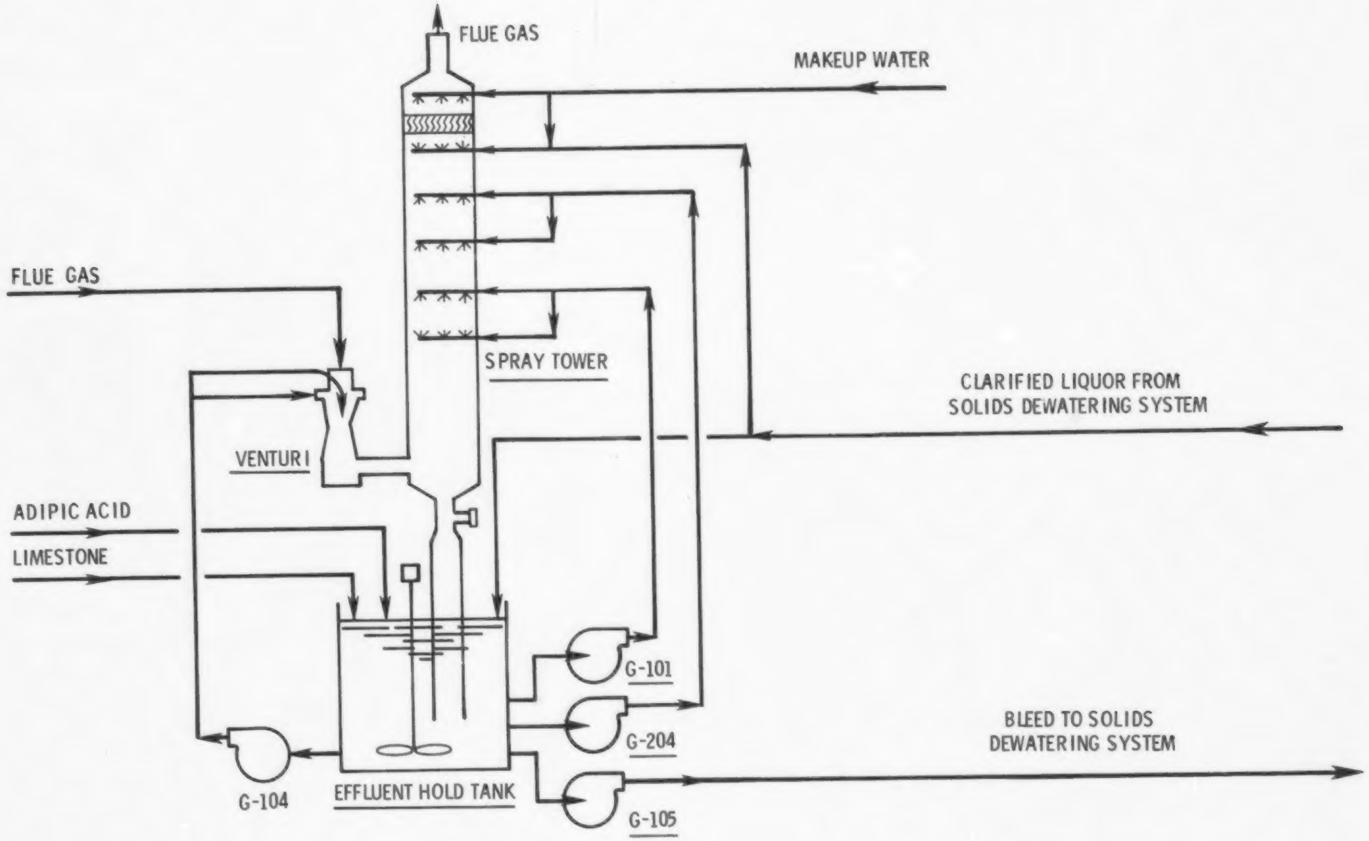

FLUE GAS
MAKEUP WATER
FLUE GAS
SPRAY TOWER
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
VENTURI
ADIPIC ACID
LIMESTONE
G-101
G-204
BLEED TO SOLIDS DEWATERING SYSTEM
G-104
EFFLUENT HOLD TANK
G-105

Figure 7-1

Flow Diagram For The One-Loop Venturi/Spray Tower System with One Tank And Without Forced Oxidation

Table 7-1

RESULTS OF ONE-SCRUBBER-LOOP VENTURI/SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS USING A SINGLE TANK WITHOUT FORCED OXIDATION

Major Test Conditions	926-1A	926-1G	926-1B	926-1C	926-1H	926-1D	926-1E
Fly ash loading	High	High	High	High	High	High	High
Gas rate, acfm @ 300°F	35,000	35,000	35,000	35,000	35,000	35,000	35,000
Venturi liquor rate, gpm	600	600	600	600	600	600	600
Spray tower liquor rate, gpm	1600	1600	1600	1600	1600	1600	1600
Percent solids recirculated (controlled)	15	15	15	15	15	15	15
EHT residence time, min	9.1	9.1	9.1	9.1	9.1	9.1	9.1
EHT tank level, ft	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Scrubber inlet pH (controlled)	4.6	4.8	4.8	5.0	5.25	5.5	5.0
Adipic acid concentration, ppm	(1)	(1)	1300	1300	1300	1300	700
Venturi pressure drop, inches H_2O	9	9	9	9	9	9	9
Run-Average Results							
Start-of-run date	12/18/79	1/3/80	1/16/80	1/24/80	1/29/80	2/8/80	2/15/80
Onstream hours	297	244	184	116	169	116	119
Percent SO_2 removal	90	91	84	91	93	96.5	77
Inlet SO_2 concentration, ppm	2650	2250	2115	2150	2150	2410	2450
Adipic acid concentration, ppm	4090	2270	1435	1290	1285	1330	735
Actual adipic acid consumption, lbs/tons SO_2 abs.	--	4.3	3.0	5.7	8.0	9.6	6.0
Adipic acid consumption ratio (actual/theor)	1.0	1.0	1.0	1.17	1.24	1.59	1.0
Percent solids recirculated	15.5	15.1	14.9	15.1	14.9	15.5	15.2
Scrubber inlet pH	4.60	4.85	4.85	5.05	5.25	5.50	5.05
Scrubber outlet pH	4.30	4.50	4.55	4.65	4.85	5.00	4.60
SO_2 make-per-pass, mmole/l	8.05	6.90	6.00	6.60	6.75	7.85	6.35
Limestone utilization, %	97	96	95	95	92	80	95
Scrubber inlet sulfite concentration, ppm	1540	875	965	325	180	135	325
Scrubber outlet sulfite concentration, ppm	1550	1440	1545	695	305	185	710
Sulfite oxidation, %	49	51	49	47	30	17	32
Scrubber inlet gypsum saturation, %	130	116	127	129	118	112	113
Centrifuge cake solids, wt%	69	70	69	66	61	60	60
Mist eliminator restriction, %	--	--	0	--	--	--	0

Notes: (1) Adipic acid concentration controlled at a level to provide 92% SO_2 removal.

concentration were varied in the tests. All other conditions were held constant.

7.2.1 Theoretical Adipic Acid Consumption Rate

The theoretical adipic acid consumption rate is defined as the rate of adipic acid leaving the scrubber system in the liquor which is entrained in the discharge sludge (filter cake, centrifuge cake, or clarifier underflow) in a closed-liquor-loop operation. The theoretical consumption rate is calculated from the material balances for solids discharged from the scrubber system, solids (or liquor) concentration in the discharged sludge, and adipic acid concentration in the liquor.

The ratio of actual to theoretical adipic acid consumption rate was calculated for each run in Table 7-1. This ratio is greater than one if there is any degradation or unaccounted loss of adipic acid.

7.2.2 Effect of pH on Adipic Acid Consumption Rate

As can be seen in Table 7-1, the ratios of actual-to-theoretical adipic acid consumption were all 1.0 at a scrubber inlet pH of 4.60 and 4.85 for Runs 926-1A, 926-1G, and 926-1B, when the adipic acid concentrations were controlled at 4090, 2270, and 1435 ppm, respectively. This indicates that there was essentially no degradation of adipic acid, within the accuracy of the material balance calculations.

Further increase in the scrubber inlet pH to 5.05, 5.25, and 5.50 during Runs 926-1C, 926-1H, and 926-1D resulted in actual-to-theoretical adipic acid consumption ratios of 1.17, 1.24, and 1.59, respectively. Run 926-1E, at 5.05 inlet pH and 735 ppm adipic acid, gave a consumption ratio of 1.0. This is lower than the consumption ratio of 1.17 for Run 926-1C at the same 5.05 pH but higher adipic acid concentration of 1290 ppm. This is reasonable to expect if the degradation of the acid is a function of concentration.

Thus, if a limestone scrubber is operated at an inlet pH below about 5.0, it is expected to have minimum adipic acid degradation. However, higher adipic acid concentrations are needed, as in Runs 926-1A and 926-1G, to achieve the same SO_2 removal efficiency.

Despite the higher adipic acid concentration required at the lower pH operation, the adipic acid consumption can be actually less, as can be seen in Table 7-1, in terms of adipic acid consumption per ton of SO_2 absorbed. For Run 926-1D at a scrubber inlet pH of 5.50 and an adipic acid concentration of 1330 ppm, the unaccounted adipic acid loss was 37 percent (i.e., of the 1.59 parts added, 0.59 part or 37 percent was unaccounted for, and 1.0 part or 63 percent was unaccounted for in the liquor of centrifuge cake), and the actual consumption was the highest at 9.6 lbs/ton SO_2 absorbed (4.9 lbs/ton limestone added).

7.2.3 Effect of pH and Adipic Acid Concentration on SO_2 Removal

Higher adipic acid concentration is required at a low pH than at a high pH to achieve similar SO_2 removal. This can be seen in the following table:

	926-1A	926-1G	926-1C	926-1H
Scrubber inlet pH	4.60	4.85	5.05	5.25
Adipic acid conc., ppm	4090	2270	1290	1285
Percent SO_2 removal	90	91	91	93
Inlet SO_2 conc., ppm	2650	2250	2150	2150
Percent limestone utilization	97	96	95	92

The optimum scrubber inlet pH appears to be 5.0 to 5.1 (Run 926-1C) where the adipic acid concentration required is only about 1300 ppm to achieve 91 percent SO_2 removal. More importantly, the adipic acid degradation is insignificant at this pH level (1.17 actual-to-theoretical consumption ratio for Run 926-1C).

Note that SO_2 removal is more sensitive to pH and inlet SO_2 concentrations at the scrubber inlet pH levels of 4.6 to 4.85 tested because the buffer capacity of adipic acid is reduced at the lower pH levels.

7.2.4 Limestone Utilization

One of the benefits of the low pH operation is that very high limestone utilization can be realized. Limestone utilizations were 95 percent or higher at the scrubber inlet pH of 5.05 or lower and 9.1 minutes residence time in the effluent hold tank.

7.2.5 Sulfite Oxidation and Centrifuge Cake Solids

Another important benefit of low pH operation is the ease of forced oxidation of sulfite. A natural oxidation level of about 50 percent was achieved at the scrubber inlet pH of 5.05 or lower, as compared to 15 to 20 percent oxidation at a normal inlet pH of about 5.5. The resulting centrifuge cake solids concentrations were almost 10 percentage points higher for the lower pH operation.

7.3 SUMMARY

The following is a summary of the test results:

- Apparent degradation of adipic acid is inhibited at low pH. Without forced oxidation, the critical pH appears to be about 5.0 at the scrubber inlet, below which degradation is minimized (actual-to-theoretical consumption ratio equals 1.0).
- Because of reduced ionization and buffer capacity of adipic acid at low pH, the required adipic acid concentration is 2 to 3 times higher at a scrubber inlet pH of 4.6 to 4.85 than at 5.05 to 5.25 to achieve a similar degree of SO_2 removal (about 91 percent)
- Operation at low pH and high adipic acid concentration results in lower adipic acid consumption than operation at high pH and low concentration.
- Other benefits obtained when the scrubber inlet pH was held at 5.05 or lower include: high limestone utilization (95 percent or higher), high natural sulfite oxidation (about 50 percent) which would facilitate

forced oxidation, and the resultant high centrifuge cake solids (near 70 percent).

- The optimum scrubber inlet pH for the one-scrubber-loop venturi/spray tower with a single-tank configuration appears to be 5.0 to 5.1 with respect to adipic acid consumption, limestone utilization, and the sensitivity of SO_2 removal to the variations in the pH and inlet SO_2 concentration.

Section 8

VENTURI SCRUBBER SO_2 REMOVAL WITH LIMESTONE/ADIPIC ACID SLURRY WITHOUT FORCED OXIDATION

A series of 12 runs (Runs 927-1A through 927-1L) was made in late-February through early-March 1980, using the venturi scrubber only to determine its maximum SO_2 removal capability with adipic acid-enhanced limestone scrubbing.

While it is recognized that SO_2 removal with the venturi alone could not meet the SO_2 emission standard for high-sulfur coal, even with very high concentrations of adipic acid, scrubbing with the venturi alone could be attractive economically for low-sulfur coal applications where only 70 percent SO_2 removal is required.

A single tank was used without forced oxidation for all tests. The flow configuration for these tests was the same as that shown in Figure 7-1, except that the slurry flow to the spray tower (Pumps G-101 and G-204) was turned off.

The slurry flow to the venturi was held constant at 600 gpm for all runs. Variables investigated were adipic acid concentration, gas rate (or venturi liquid-to-gas ratio at a constant slurry rate), venturi pressure drop, and inlet pH. Operating conditions common for all runs were:

Fly ash loading:	High (2-7 grains/dry scf)
Effluent hold tank level:	8.5 ft
Effluent hold tank residence time:	33.4 minutes
Slurry solids concentration:	15 percent
Solids dewatering equipment:	Clarifier and centrifuge

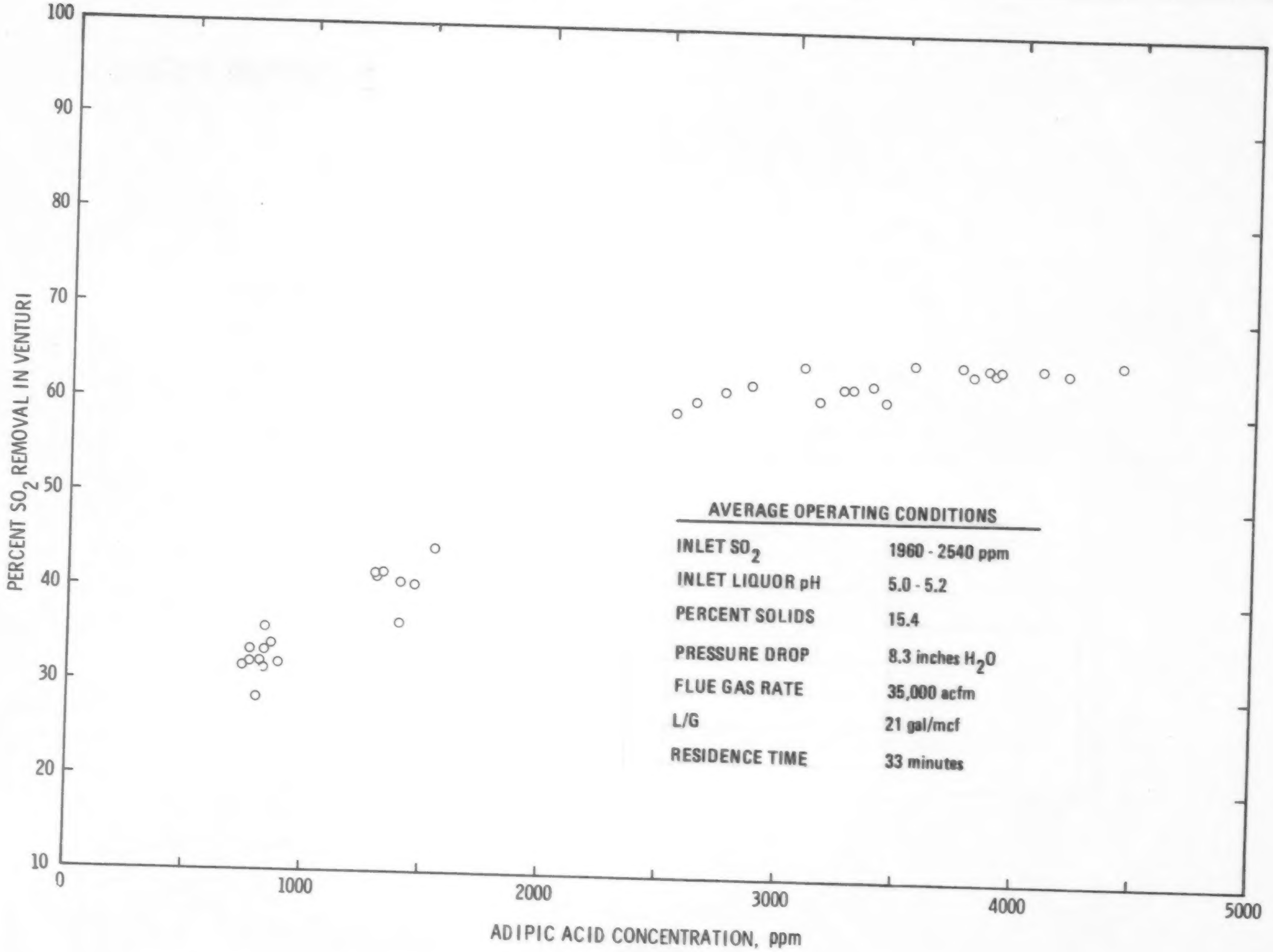


Figure 8-1
Venturi SO_2 Removal vs. Adipic Acid Concentration
During Limestone Runs 927-1A, 1D And 1E

8.1 DISCUSSION OF TEST RESULTS

Table 8-1 summarizes the major test conditions and the run-average test results.

8.1.1 Effect of Adipic Acid Concentration

Runs 927-1A, 927-1D, and 927-1E were all operated at a gas rate of 35,000 acfm (@ 300°F), a liquid-to-gas ratio of 21 gal/mcf, and a venturi inlet pH of 5.1. Although 6 inches H_2O pressure drop across the venturi was specified, a minimum pressure drop of about 8.3 inches was obtained for these runs because of a problem in the adjustable plug mechanism. Average SO_2 removal increased from 34 to 41 and 65 percent when the adipic acid concentration was raised from 815 to 1335 and 3985 ppm, respectively. Hourly SO_2 removal data for these 3 runs are plotted in Figure 8-1. It appears that the SO_2 removal levels off at about 65 percent, suggesting that the overall rate of SO_2 absorption may have been limited by the gas-phase mass transfer above 3500 ppm adipic acid.

8.1.2 Effect of Liquid-to-Gas Ratio

During Runs 927-1B, 927-1C, and 927-1G, the liquid-to-gas ratio was increased to 37 gal/mcf. Average SO_2 removal increased only marginally to 39, 47, and 68 percent, respectively. For these runs, adipic acid concentrations were 705, 1360, and 4030 ppm, respectively. The scrubber inlet pH was 5.1, actual venturi pressure drop was 6 inches H_2O, and the average inlet SO_2 concentration ranged from 2470 to 2790 ppm.

Although SO_2 removal was below 70 percent with high inlet SO_2 concentration,

Table 8-1

RESULTS OF VENTURI LIMESTONE/ADIPIC ACID TESTS USING A SINGLE TANK WITHOUT FORCED OXIDATION

Major Test Conditions	927-1A	927-1B	927-1J	927-1C	927-1D	927-1E	927-1F	927-1G	927-1H	927-1I	927-1K	927-1L
Fly ash loading	High	High	High	High	High	High	High	High	High	High	High	High
Gas rate, acfm @ 300°F	35,000	20,000	27,500	20,000	35,000	35,000	27,500	20,000	27,500	27,500	27,500	20,000
Venturi liquor rate, gpm	600	600	600	600	600	600	600	600	600	600	600	600
Percent solids recirculated (controlled)	15	15	15	15	15	15	15	15	15	15	15	15
EHT residence time, min	33.4	33.4	33.4	33.4	33.4	33.4	33.4	33.4	33.4	33.4	33.4	33.4
EHT tank level, ft	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Venturi inlet liquor pH (controlled)	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	4.8	4.8
Adipic acid concentration, ppm	700	700	700	1300	1300	4000	4000	4000	4000	4000	4000	4000
Venturi pressure drop, inches H_2O	6	6	6	8	6	6	6	6	9	12	9	8
Run-Average Results												
Start-of-run date	2/20/80	2/22/80	2/22/80	2/24/80	2/26/80	2/27/80	3/1/80	3/1/80	3/2/80	3/2/80	3/4/80	3/5/80
Onstream hours	43	24	24	48	27	69	26	13	13	21	32	16
Percent SO_2 removal	34	39	33	47	41	65	67(1)	68	69	65	59	62
Inlet SO_2 concentration, ppm	1990	2470	2390	2595	2445	2360	2255	2790	3030	2945	2245	2100
Adipic acid concentration, ppm	815	705	795	1360	1335	3985	3990	4030	4005	4015	4050	4340
Scrubber percent solids recirculated	14.6	14.5	14.6	14.0	16.3	15.4	15.3	14.3	15.0	15.3	14.8	13.6
Scrubber inlet pH	5.05	5.15	5.10	5.15	5.15	5.10	5.10	5.05	5.10	5.10	4.85	4.80
Sulfite concentration in inlet liquor, ppm	365	365	110	320	255	295	460	235	885	665	910	1010
SO_2 Make-per-pass, mmole/l	8.35	6.80	7.65	8.65	12.4	19.0	14.7	13.4	20.3	18.4	12.9	9.20
Limestone utilization, %	92	92	91	91	83	85	85	86	88	91	93	90
Sulfite oxidation, %	36	34	29	32	32	28	23	22	20	32	26	30
Inlet liquor gypsum saturation, %	115	115	135	120	120	125	130	185	125	120	140	125
Centrifuge cake solids, wt%	66	67	68	66	68	61	63	63	63	63	65	68
Mist eliminator restriction, %	--	--	--	--	--	--	--	--	--	--	--	--
Venturi pressure drop, inches H_2O	8.2	5.9	5.9	6.0	8.4	8.3	5.9	6.0	8.7	11.1	8.8	6.2

Note: (1) SO_2 removal dropped to 60% when inlet SO_2 concentration increased to 2870 ppm under replicate conditions.

the venturi-only mode of operation with limestone/adipic acid slurry may be viable for low-sulfur coal applications where inlet SO_2 concentrations are less than 1000 ppm.

8.1.3 Effect of Venturi Pressure Drop

During Runs 927-1F, 927-1H, and 927-1I, the venturi pressure drop was 5.9, 8.7, and 11.1 inches H_2O, respectively. For these runs, adipic acid concentration was maintained at 4000 ppm, liquid-to-gas ratio was controlled at 27 gal/mcf, and the inlet pH was controlled at 5.1. SO_2 removal was 60 percent at 5.9 inches H_2O pressure drop, and appeared to level off at 65 to 69 percent at 8.7 and 11.1 inches H_2O.

8.1.4 Effect of Venturi Inlet pH

Run 927-1K was made under the same conditions as Run 927-1H, except for the scrubber inlet pH. SO_2 removal increased significantly from 59 percent at 2245 ppm inlet SO_2 concentration and at 4.85 inlet pH to 69 percent at 3030 ppm inlet SO_2 concentration and at 5.10 inlet pH. Similar sensitivity of SO_2 removal to pH can be observed by comparing Runs 927-1G and 927-1L.

8.2 SUMMARY

Based on the test results, the following conclusions can be made:

- At a liquid-to-gas ratio of 21 gal/mcf, a venturi inlet pH of 5.1, and a venturi pressure drop of 8.3 inches H_2O, SO_2 removal appears to level off at 65 percent above 3500 ppm adipic acid. (SO_2 removals greater than 65 percent may be possible at pH higher than 5.1).

- Increasing the liquid-to-gas ratio to 37 gal/mcf (with a somewhat reduced pressure drop of 6 inches H_2O) improves SO_2 removal marginally.

- With low-sulfur coals producing less than 1000 ppm inlet SO_2 concentration, 70 percent SO_2 removal should be achievable at 5.1 inlet pH, 4000 ppm adipic acid, 6 to 8 inches H_2O pressure drop, and 21-37 gal/mcf liquid-to-gas ratio.

- SO_2 removal is sensitive to inlet pH (4.8 to 5.1) and adipic acid concentration (700 to 3500 ppm) but is insensitive to liquid-to-gas ratio (21 to 37 gal/mcf) and venturi pressure drop (6 to 11 inches H_2O).

Section 9

VENTURI/SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND ONE-TANK FORCED OXIDATION

Following the venturi-only testing discussed in the last section, the venturi/spray tower system was modified to allow testing in a single tank mode with forced oxidation in the tank. A total of 7 runs were made from mid-March to early-April 1980, including 4 runs operated with the venturi only.

Although sufite oxidation of 99 percent or higher was achieved for the runs with forced oxidation, limestone blinding was encountered as was evidenced by poor limestone utilization. The long (50 ft) crossover line which routed the venturi and spray tower effluent slurries to the oxidation tank apparently behaved as an effective plug-flow reactor which facilitated calcium sulfite precipitation. The precipitation occurred preferentially on the alkaline limestone particles in the effluent slurry, because the slurry was deficient in calcium sulfite solid crystal seeds due to oxidation.

9.1 SYSTEM DESCRIPTION

Figure 9-1 is a schematic flow diagram of the venturi/spray tower system using a single tank (D-208) in which compressed air was injected through a 3-inch diameter open-ended pipe ell. The venturi and spray tower effluent slurries were routed to the oxidation tank via a 16-inch diameter crossover line about 50 ft long. This crossover line was operated full of slurry (490 gallons) because nearly its entire length was below the oxidation tank liquid level.

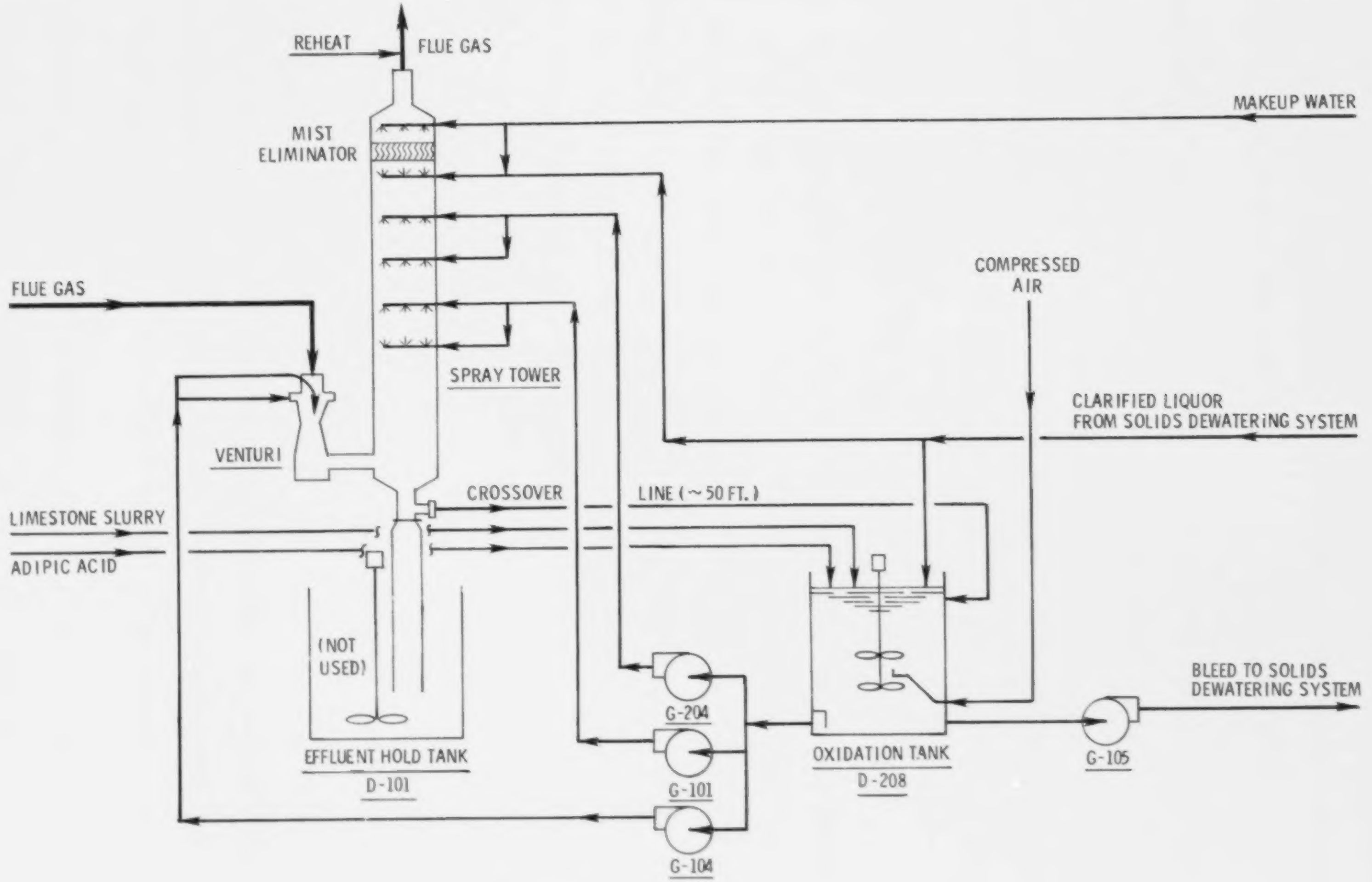

REHEAT
FLUE GAS
MAKEUP WATER
MIST ELIMINATOR
FLUE GAS
COMPRESSED AIR
SPRAY TOWER
CLARIFIED LIQUOR FROM SOLIDS DEWATERiNG SYSTEM
VENTURI
CROSSOVER
LINE (~50 FT.)
LIMESTONE SLURRY
ADIPIC ACID
(NOT USED)
BLEED TO SOLIDS DEWATERING SYSTEM
G-204
G-101
G-104
G-105
EFFLUENT HOLD TANK
D-101
OXIDATION TANK
D-208

Figure 9-1

Flow Diagram For The One-Loop Venturi/Spray Tower System
With One Tank And Forced Oxidation

The line acted as a plug-flow reactor as previously mentioned. It is emphasized that this setup was necessitated by the limited availability of space and was unique to the Shawnee Test Facility.

A severe cavitation problem in the slurry recirculation pumps during initial startup was solved by installing a baffle near the pump suction nozzles and by moving the air injection point higher, to between the two agitator turbines. Both turbines propel the slurry downward. Figure 9-2 shows the arrangement of the modified oxidation tank.

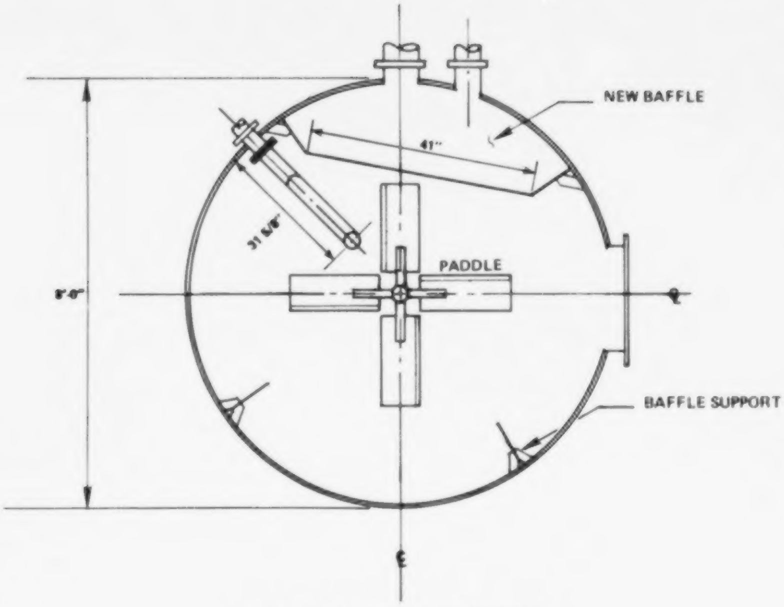
9.2 DISCUSSION OF TEST RESULTS

Tables 9-1 and 9-2 summarize the results of the single-tank forced oxidation tests with both the venturi and the spray tower in operation, and with the venturi alone, respectively. The initial test plan called for variations of the scrubber inlet pH and adipic acid concentration, to observe the effects on adipic acid consumption under forced oxidation conditions for comparison with similar runs made without forced oxidation (see Section 7). However, the original test objectives were modified in favor of a more thorough study of the limestone blinding phenomenon when it was encountered.

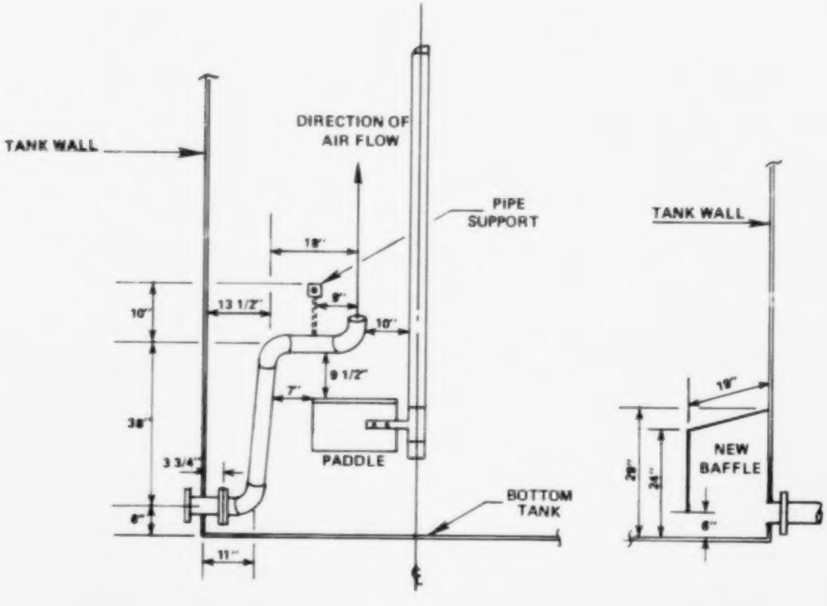
9.2.1 Initial Tests

In Run 914-1A, a total slurry flow rate of 2200 gpm resulted in 2.9 minutes residence time in the oxidation tank (Table 9-1), 98.7 percent sulfite oxidation in the solids, high inlet liquor sulfite concentration (1250 ppm), and poor limestone utilization of 46 percent despite a low scrubber inlet pH of 4.6.

To reduce the high inlet liquor sulfite concentration, Run 914-1B was first run at higher pH (5.1 vs. 4.6) and then at increased oxidation intensity (air


NEW BAFFLE
41"
31 5/8"
PADDLE
8'-0"
℄
BAFFLE SUPPORT
℄

OVERHEAD VIEW OF TANK BOTTOM


TANK WALL
DIRECTION OF AIR FLOW
PIPE SUPPORT
18"
10"
13 1/2"
9"
10"
38"
9 1/2"
7"
3 3/4"
PADDLE
6"
BOTTOM TANK
11"
℄
TANK WALL
18"
NEW BAFFLE
29"
24"
6"

SIDE VIEW

SIDE VIEW

Figure 9-2

Arrangement Of Modified Venturi/Spray Tower Oxidation Tank (D-208)

Table 9-1

RESULTS OF ONE-SCRUBBER-LOOP VENTURI/SPRAY TOWER
LIMESTONE/ADIPIC ACID TESTS WITH ONE TANK AND FORCED OXIDATION

Major Test Conditions	914-1A	914-1B	914-1C
Fly ash loading	High	High	High
Gas rate, acfm @ 300°F	35,000	35,000	35,000
Venturi liquor rate, gpm	600	600	600
Spray tower liquor rate, gpm	1600	1600	1600
Percent solids recirculated (controlled)	15	15	15
Oxidation tank Residence time, min	2.9	2.9	2.9
Oxidation tank Level, ft	17	17	17
Scrubber inlet pH (controlled)	4.6	5.1	4.6
Adipic acid concentration, ppm	4000	4000	4000
Air rate to oxidizer, scfm	200	200/300	0
Venturi pressure drop, inches H_2O	9	9	9
Run-Average Results			
Start-of-run date	3/13/80	3/19/80	4/7/80
Onstream hours	105	11	47
Percent SO_2 removal	91.6	(1)	92.6
Inlet SO_2 concentration, ppm	1980		1955
Adipic acid concentration, ppm	4040		4225
Adipic acid consumption ratio (actual/theor.)	3.41		1.59
Actual acipid acid consumption, lbs/ton SO_2 absorbed	64.1		43.3
Percent solids recirculated	15.9		14.9
Scrubber inlet pH	4.60		4.66
Sulfite concentration in inlet liquor, ppm	1250		862
SO_2 make-per-pass, mmole/l	6.1		6.1
Limestone utilization, %	46		93
Sulfite oxidation, %	98.7		32
Gypsum saturation in inlet liquor, %	145		120
Centrifuge cake solids, wt%	79		65
Air stoichiometry, atom O/mole SO_2 abs.	1.9		0
Mist eliminator restriction, %	--		3

(1) No steady state was established due to severe limestone blinding.

rate 300 scfm vs. 200 scfm). However, no indication of increased limestone utilization was noted and the run was terminated.

9.2.2 Venturi-Only Test

The low oxidation tank residence time of 2.9 minutes was increased to 10.6 minutes during Runs 927-1M, 927-1N, and 927-10 (Table 9-2) by operation of the venturi only (600 gpm). This necessarily raised the SO_2 make-per-pass to 17.1 m-moles/liter (Run 927-1M) which was reduced to 11.1 m-moles/liter in Run 927-1N by reducing the gas rate. The limestone utilization was still low and a run at a controlled limestone stoichiometry of 1.2 (Run 927-10) confirmed that limestone blinding was occurring in the crossover line because the scrubber inlet pH of 4.55 was lower than expected. This line was in effect a 50-second (490 gallons) residence time plug-flow reactor to which was fed slurry depleted in calcium sulfite seed crystals and in which a favorable environment was provided for the liquor sulfite to precipitate on limestone particles before reaching the oxidation tank.

9.2.3 Base Case Tests Without Oxidation

Run 927-1P was made under the same conditions as Run 927-1M except that the air to the oxidizer was shut off to provide a base case run without forced oxidation. Limestone utilization remained poor (54 percent) due to the combined effect of continued high SO_2 make-per-pass (16.4 m-moles/liter) and long residence time (nearly 50 seconds) in the crossover line.

Run 914-1C was made under the same conditions as Run 914-1A except without forced oxidation. With an SO_2 make-per-pass of only 6.1 m-moles/liter and 13 seconds residence time in the crossover line, combined with sufficient calcium sulfite solid crystal seeds (32 percent oxidation), limestone utilization

Table 9-2

RESULTS OF VENTURI LIMESTONE/ADIPIC ACID TESTS WITH ONE TANK AND FORCED OXIDATION

Major Test Conditions	927-1M	927-1N	927-1O	927-1P
Fly ash loading	High	High	High	High
Gas rate, acfm @ 300°F	30,000	20,000	20,000	30,000
Venturi liquor rate, gpm	600	600	600	600
Percent solids recirculated (controlled)	15	15	15	15
Oxidation tank residence time, min	10.6	10.6	10.6	10.6
Oxidation tank level, ft	17	17	17	17
Venturi inlet liquor pH (controlled)	5.0	5.0	--	5.0
Venturi inlet liquor limestone stoichiometry (controlled)	--	--	1.2	--
Adipic acid concentration, ppm	4000	4000	4000	4000
Air rate to oxidizer, scfm	300	300	300	0
Venturi pressure drop, inches H_2O	9	9(1)	9(1)	9
Run-Average Results				
Start-of-run date	3/21/80	3/26/80	3/30/80	4/2/80
Onstream hours	115	13	75	108
Percent SO_2 removal	71.5	77.4	67.4	69.6
Inlet SO_2 concentration, ppm	2260	2030	2070	2225
Adipic acid concentration, ppm	4170	3960	4130	3960
Adipic acid consumption ratio (actual/theor.)	2.19	3.0	1.93	2.26
Actual acipic acid consumption, lbs/ton SO_2 absorbed	32.0	50.8	28.6	62.5
Percent solids recirculated	15.0	16.1	15.0	14.9
Scrubber inlet pH	5.05	5.15	4.55	5.07
Sulfite concentration in inlet liquor, ppm	75	44	28	349
SO_2 make-per-pass, mmole/l	17.1	11.1	9.9	16.4
Limestone utilization, %	50	35	85	54
Sulfite oxidation, %	99.4	99.2	99.2	23
Gypsum saturation in inlet liquor, %	105	105	110	125
Centrifuge cake solids, wt%	78	79	78	63
Air stoichiometry, atom O/mole SO_2 abs.	3.8	5.9	6.6	0
Mist eliminator restriction, %	--	--	--	--

(1) Actual pressure drop was about 7 inches H_2O because of a problem with the adjustable plug mechanism and low gas flow rate.

improved to 93 percent.

9.2.4 Effect of pH and Limestone Utilization on Adipic Acid Consumption

It was mentioned in Section 7 that essentially no degradation of adipic acid occurs at a scrubber inlet pH below 5.0 when oxidation is not forced. No limestone blinding was encountered in those tests. In these tests adipic acid degradation appeared to increase with forced oxidation. In addition, it was observed that poor limestone utilization increased the degradation. These observations are more clearly seen in the following table:

	927-1M	927-IN	927-10
Venturi inlet pH	5.05	5.15	4.55
Percent limestone utilization	50	35	85
Adipic acid consumption ratio (Actual/Theoretical)	2.19	3.0	1.93
Percent unaccounted loss of adipic acid	54.3	66.7	48.2
Actual adipic acid consumption, lb/ton SO_2 absorbed	32.0	50.8	28.6
Unaccounted adipic acid loss, lb/ton SO_2 absorbed	17.4	33.9	13.8

Note that the adipic acid consumption ratios in these runs were significantly higher than in those without forced oxidation (see Table 7-1).

9.3 SUMMARY

Limestone blinding caused by the 50-ft long crossover line was encountered in most of the runs. The phenomenon of limestone blinding is discussed in more detail in Section 25.

The following is a summary of the test results and findings:

- Good sulfite oxidation of 99 percent or higher was achieved in the solids despite poor limestone utilization.

- Limestone blinding occurred in the 50-ft long crossover line which transferred the venturi and spray tower effluent slurries to the oxidation tank and which behaved as an effective plug-flow reactor for calcium sulfite precipitation. This peculiarity in flow configuration was unique to the Shawnee Test Facility.

- Limestone blinding caused by the long crossover line and high SO_2 make-per-pass could not be prevented by increasing the oxidation intensity in the oxidation tank to reduce the sulfite concentration in the scrubber inlet liquor, even at SO_2 make-per-pass values as low as 6.1 m-moles/liter, and was compounded by depletion of calcium sulfite seed crystals in the scrubber effluent.

- Actual-to-theoretical adipic acid consumption ratio and total actual adipic acid requirement (pounds per ton SO_2 absorbed) increased with forced oxidation, increasing pH, and decreasing limestone utilization.

Section 10

VENTURI/SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND TWO-TANK FORCED-OXIDATION

Operation with two tanks in series, with forced oxidation in the first tank and limestone added to the second tank, has several advantages over the single-tank operation with forced oxidation (see Section 9):

- Lower pH in the first tank (oxidation tank), which receives the scrubber effluent slurry, gives better oxidation efficiency.
- The potential of limestone blinding by calcium sulfite is reduced because liquor sulfite is oxidized in the first tank before fresh limestone is added to the second tank.
- Limestone utilization is improved with two tanks in series.
- The second tank offers extra time for gypsum desupersaturation and precipitation.
- The second tank provides air-free suction for slurry recirculation pumps.

Earlier test results from the TCA system in May and October 1979 with limestone/adipic acid and forced oxidation have shown two-tank operation to be superior to the single-tank mode (see Section 18). Eight runs (Runs 916-1A through 916-1H) were made on the one-loop venturi/spray tower system using two tanks in series from late-April to late-May 1980.

10.1 SYSTEM DESCRIPTION

Figure 10-1 shows a schematic flow diagram of the venturi/spray tower system using two tanks. Air was injected into the first tank (D-208) while limestone

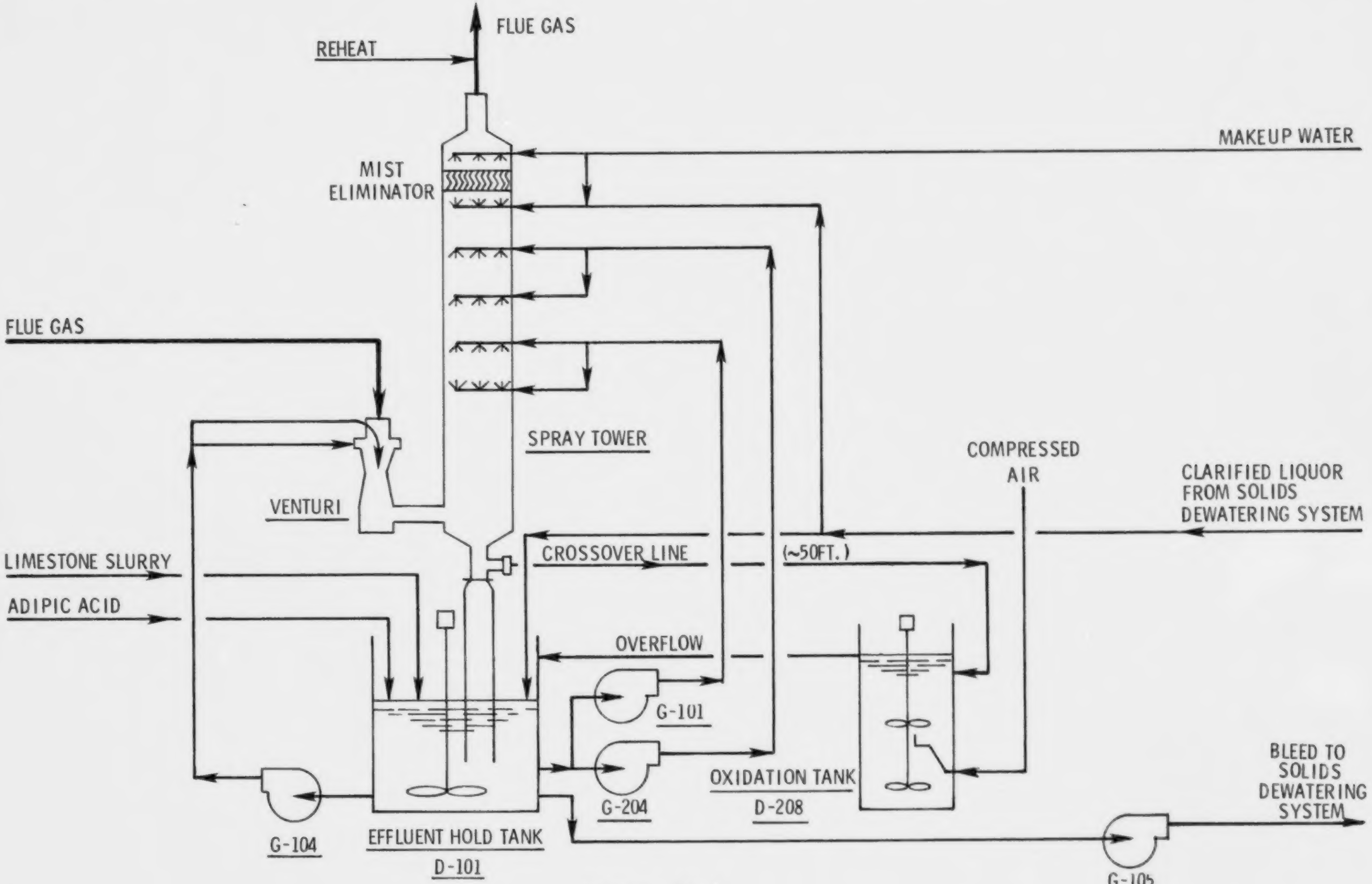

FLUE GAS
REHEAT
MAKEUP WATER
MIST ELIMINATOR
FLUE GAS
SPRAY TOWER
COMPRESSED AIR
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
VENTURI
LIMESTONE SLURRY
CROSSOVER LINE
(~50FT.)
ADIPIC ACID
OVERFLOW
G-101
BLEED TO SOLIDS DEWATERING SYSTEM
OXIDATION TANK
D-208
G-204
G-104
EFFLUENT HOLD TANK
D-101
G-105

Figure 10-1

Flow Diagram For The One-Loop Venturi/Spray Tower System
With Two Tanks And Forced Oxidation

and adipic acid were added to the second tank (D-101). The detailed arrangement of the oxidation tank (8 ft diameter) is shown in Figure 9-2.

10.2 DISCUSSION OF TEST RESULTS

Table 10-1 summarizes the results of the eight runs made with two tanks in series, including one run (Run 916-1H) without forced oxidation. In general, good SO_2 removal was achieved with excellent oxidation of the solids for all the forced oxidation tests. However, as in the tests with forced oxidation using a single tank (see Section 9), calcium sulfite blinding of limestone in the crossover line continued to reduce the limestone utilization below the level normally expected with two-tank operation. This remained true despite the efforts to reduce limestone blinding by either increasing the oxidation intensity or lowering the SO_2 make-per-pass.

During the testing with forced oxidation (Runs 916-1A through 916-1G), several measures were taken to eliminate or minimize the effect of the long crossover line. Operating parameters explored included:

- Liquid-to-gas ratios in the spray tower of 17.8 to 100 gal/mcf
- SO_2 make-per-pass of 3.6 to 12.0 m-moles/liter
- Adipic acid concentrations of 1490 to 4015 ppm
- Scrubber inlet pH of 4.77 to 5.33
- Air stoichiometry to the oxidizer of 1.5 to 2.5 atoms O/mole SO_2 absorbed

However, the overriding tendency of the crossover line to act as a plug-flow reactor, as described in Section 9, could not be eliminated.

Table 10-1

RESULTS OF ONE-SCRUBBER-LOOP VENTURI/SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS WITH TWO TANKS AND FORCED OXIDATION

Major Test Conditions	916-1A	916-1B	916-1C	916-1D	916-1E	916-1F	916-1G	916-1H
Fly ash loading	High	High	High	High	High	High	High	High
Flue gas rate, acfm @ 300°F	35,000	30,000	30,000	30,000	20,000	30,000	30,000	30,000
Venturi liquor rate, gpm	600	600	600	600	600	600	600	600
Spray tower liquor rate, gpm	500	1200	1200	1200	1600	1200	1200	1200
Percent solids recirculated (controlled)	15	15	15	15	15	15	15	15
EHT res. time (min)/tank level (ft)	18.2/8.5	11.1/8.5	11.1/8.5	11.1/8.5	9.1/8.5	11.1/8.5	11.1/8.5	11.1/8.5
Oxid. tk. res. time (min)/tank level (ft)	6.1/18	3.8/18	3.8/18	3.8/18	3.1/18	3.8/18	3.8/18	3.8/18
Inlet liquor pH (controlled)	4.8	4.8	4.8	5.1	5.1	5.4	5.4	5.1
Adipic acid concentration, ppm	4000	4000	4000/1500	1500	1500	1500	1500	1500
Air stoich. to oxidizer, atom O/mole SO_2 absorbed	1.5	1.5	1.5	1.5	1.5	1.5	2.5	0
Venturi pressure drop, inches H_2O (1)	9	6	6	6	7	6	6	6
Run-Average Results								
Start-of-run-date	4/24/80	4/28/80	5/2/80	5/6/80	5/13/80	5/19/80	5/22/80	5/24/80
Onstream hours	89	77	92	163	145	71	61	84
Percent SO_2 removal	88.1	96.5	93.7 → 91.2	92.4	98.0	89.2	93.7	85.5
Inlet SO_2 concentration, ppm	2010	2170	2330	2220	1880	2260	2150	2500
Adipic acid concentration, ppm	3990	4015	3450/1600	1490	1540	1510	1550	1440
Adipic acid consumption ratio, (actual/theor)	2.84	1.37	--	--	4.89	2.30	3.32	2.03
Actual adipic acid consumption, lbs/ton SO_2 abs.	32.7	15.8	--	--	8.91	7.75	8.76	11.4
Percent solids recirculated	15.7	15.3	15.1	15.0	14.9	15.9	15.6	15.6
Scrubber inlet pH	4.77	4.83	4.86	5.12	5.13	5.14	5.33	5.12
Oxidation tank pH	4.52	4.70	4.67	5.03	5.09	5.06	5.24	4.77
Limestone utilization, %	70	84	88	72	86	46	61	96
Sulfite oxidation, %	99.4	99.7	99.7	99.8	99.5	99.4	99.6	50.4
Inlet liquor gypsum saturation, %	120	105	110	105	105	145	120	120
Sulfite conc. in inlet liquor, ppm	380	71	137	81	60	583	33	317
Avg. air flow rate, scfm	151	158	158	150	90	148	246	0
Centrifuge cake solids, %	79	76	34(2)	84(3)	88(3)	84(3)	85(3)	59(3)
Mist eliminator restriction, %	--	1	--	--	--	--	--	1
SO_2 make-per-pass, m-mole/liter	12.0	7.4	7.5-7.7	7.3	3.6	7.1	7.1	7.6

(1) Venturi operated with plug wide open for all runs except for Run 916-1A where pressure drop was controlled at 9 inches H_2O.

(2) System operated with clarifier only.

(3) Drum filter used in place of centrifuge.

10.2.1 Initial Tests

Run 916-1A was originally scheduled to operate with 1600 gpm spray tower slurry flow rate. However, increasing the oxidation tank level from 17 ft (for single-tank operation) to 18 ft, to allow overflow to the effluent hold tank, caused a drop in the available head. As a result, the slurry flow in the long crossover line backed up into the spray tower and flooded the spray tower bottom.

Consequently, Run 916-1A was made with only 500 gpm slurry flow rate to the spray tower, corresponding to a spray tower liquid-to-gas ratio of 17.8 gal/mcf. At this low liquid-to-gas ratio, the SO_2 removal was 88.1 percent and the SO_2 make-per-pass was high at 12.0 m-moles/liter. Adipic acid concentration was maintained at 4000 ppm. Sulfite oxidation was excellent at 99.4 percent with a controlled air stoichiometry of 1.5 atoms oxygen/mole SO_2 absorbed.

Limestone utilization was poor at 70 percent with a scrubber inlet pH of only 4.77 and with two-tank operation. This was again caused by limestone blinding in the long crossover line, described in Section 9, at the high SO_2 make-per-pass and about 27 seconds residence time in the line (490 gallons at 1100 gpm total flow).

The poor limestone utilization, together with forced oxidation, resulted in a fairly high actual-to-theoretical adipic acid consumption ratio of 2.84 (64.8 percent unaccounted loss) and an actual consumption of 32.7 lb/ton SO_2 absorbed (14.6 lb/ton limestone).

In the second run, Run 916-1B, the test conditions were set at 30,000 acfm gas rate @ 300°F and 600/1200 gpm slurry flow rates to the venturi/spray tower. The venturi plug was operated wide open to give a higher absolute pressure within the spray tower for easier gravity draining of the 1800 gpm total slurry flow. This resulted in a pressure drop of 6 inches H_2O across the venturi. The combination of 30,000 acfm flue gas and 1200 gpm slurry rate provided a liquid-to-gas ratio of 50 gal/mcf in the spray tower. It was felt that further reduction in flue gas rate (but at a higher spray tower slurry rate) would lower the scrubber's rating as a 10-MW prototype unit.

The increase in the spray tower liquid-to-gas ratio in Run 916-1B increased both the SO_2 removal and the limestone utilization to 96.5 and 84 percent, respectively. The SO_2 make-per-pass decreased to only 7.4 m-moles/liter and the residence time in the long crossover line decreased to about 16 seconds. These probably resulted in the improved limestone utilization of 84 percent. However, some limestone blinding was still indicated as the utilization was still lower than what would be expected for two-tank operation at the low scrubber inlet pH of 4.83.

The improvement in limestone utilization resulted in an adipic acid consumption ratio of only 1.37 (27 percent unaccounted loss) and an actual consumption of 15.8 lb/ton SO_2 absorbed (8.5 lb/ton limestone).

10.2.2 Effect of Adipic Acid Concentration

Since later tests in this test series were scheduled using only 1500 ppm of adipic acid at higher scrubber inlet pH of 5.1 or 5.4, Run 916-1C was used to monitor SO_2 removal as the adipic acid concentration was allowed to deplete from 4000 ppm to 1500 ppm (no adipic acid addition during the run). The clarifier alone was used to speed up the depletion of the acid. Other test conditions for Run 916-1C were the same as Run 916-1B.

The SO_2 removal during Run 916-1C did not change appreciably, dropping from 93.7 to 91.2 percent as the adipic acid concentration decreased from 3450 to 1600 ppm. The average scrubber inlet pH was 4.86 and the average inlet SO_2 concentration was 2330 ppm. Limestone utilization was 88 percent which was not significantly different from Run 916-1B and indicated that some blinding still existed.

Because of the unsteady-state operation with respect to adipic acid, the material balance calculations for adipic acid were not performed for Run 916-1C.

10.2.3 Effect of Scrubber Inlet pH

During Run 916-1D, the scrubber inlet pH was raised from 4.8 to 5.1 while maintaining the adipic acid concentration at 1500 ppm. The vacuum drum filter was put in service in series with the clarifier. Other conditions were unchanged from Run 916-1C.

With the higher pH and lower adipic acid concentration, SO_2 removal remained high at 92.4 percent. However, limestone utilization dropped to only 72 percent indicating increased limestone blinding at the higher pH. No material balance calculations were made for Run 916-1D because of unsteady-state operation during the first part of the run when adipic acid was allowed to deplete from 1600 ppm to the specified 1500 ppm.

In Run 916-1F, an attempt was made to further increase the scrubber inlet pH to 5.4 with other conditions the same as Run 916-1D. Because of severe limestone blinding, the actual scrubber inlet pH was only 5.14 and the limestone utilization dropped to a low of 46 percent. Sulfite concentration in the scrubber inlet liquor increased to 583 ppm. Because of the higher concentration of limestone and correspondingly reduced gypsum seeds in the slurry, gypsum saturation increased to 145 percent in the scrubber inlet liquor.

10.2.4 Effect of SO_2 Make-Per-Pass

Because of the persistent limestone blinding in the long crossover line, Run 916-1E was made at a reduced SO_2 make-per-pass to observe whether reduced sulfite saturation (or sulfite concentration) in the scrubber effluent liquor would decrease the calcium sulfite precipitation potential, thereby reducing or eliminating the limestone blinding problem.

The SO_2 make-per-pass was reduced by decreasing the gas rate from 30,000 acfm to 20,000 acfm and by increasing the spray tower slurry flow from 1200 gpm to 1600 gpm. Other test conditions were unchanged from Run 916-1D.

The SO_2 removal was 98 percent at an average inlet SO_2 concentration of 1880 ppm, resulting in a very low SO_2 make-per-pass of 3.6 m-moles/liter. The limestone utilization did improve from 72 to 86 percent.

At the average scrubber inlet pH of 5.13 and 86 percent limestone utilization, Run 916-1E had a rather high actual-to-theoretical adipic acid consumption ratio of 4.89 (80 percent unaccounted loss), even though the actual adipic acid consumption was only 8.91 lb/ton SO_2 absorbed (4.90 lb/ton limestone). It is possible that the lower waste sludge discharge rate (because of lower gas rate) increased the adipic acid retention time and degradation in the system resulting in a higher percentage of unaccounted loss.

10.2.5 Effect of Air Stoichiometry

The air stoichiometry was increased from 1.5 to 2.5 atoms oxygen/mole SO_2 absorbed during Run 916-1G in an attempt to reduce the sulfite concentration and sulfite saturation in the scrubber inlet liquor. It was hoped that this would also reduce the sulfite saturation in the scrubber effluent liquor and, at least partially, eliminate the limestone blinding problem in the long crossover line.

Sulfite concentration in the scrubber inlet liquor dropped to a low of 33 ppm and the limestone utilization increased from 46 percent to 61 percent. Thus, the limestone blinding in the crossover line was only partially eliminated at the higher air stoichiometry.

10.2.6 Base Case Test Without Forced Oxidation

Run 916-1H was made under the same conditions as Run 916-1D except that the air to the oxidizer was turned off. Significantly, the limestone utilization improved to 96 percent because sufficient calcium sulfite solid seeds were available (50.4 percent oxidation) and blinding of limestone by calcium sulfite in the crossover line was eliminated.

10.3 SUMMARY

As in the operation using a single tank (Section 9), limestone blinding caused by the 50-ft long crossover line was encountered in most of the runs. Section 25 presents details of the limestone blinding phenomenon and the means of avoiding or eliminating it.

The following is a summary of the test results:

- Good SO_2 removal and excellent sulfite oxidation (99.4 to 99.8 percent) were achieved with the two-tank forced oxidation system.

- Limestone utilization for the two-tank operation was higher than for single-tank operation (Section 9) but below that expected with two-tank operation without limestone blinding.

- As in the single-tank operation with forced oxidation (Section 9), limestone blinding caused by the crossover line and high SO_2 make-per-pass could not be completely eliminated by increasing the oxidation intensity to reduce sulfite concentration in the scrubber inlet liquor.

- Reducing the SO_2 make-per-pass (Run 916-1E), and hence the scrubber effluent sulfite concentration, improved limestone utilization, but not to the expected level.

Section 11

BLEED STREAM OXIDATION OF LIMESTONE/ADIPIC ACID SLURRY FROM THE VENTURI/SPRAY TOWER SYSTEM

The bleed stream oxidation would be attractive for retrofit forced-oxidation installation where only an oxidation tank and the ancillary air sparging system and air compressor need be installed as add-on equipment.

Two series of tests with forced oxidation on the limestone/adipic acid bleed slurry from the venturi/spray tower system were conducted: a five-run series (Runs 909-1A through 913-1A) at high pH and low adipic acid concentration in April 1979 when the trap-out funnel in the spray tower was in place, and a three-run series (Runs 915-1A through 915-1C) at low pH and high adipic acid concentration in April 1980 after the trap-out funnel had been removed.

The former tests were conducted when it was thought that the buffering capability of adipic acid might maintain a sufficiently low pH in the oxidation tank to allow good oxidation. The latter tests were made at a time when low pH operation with adipic acid was being emphasized. It was believed that the low pH slurry from the scrubber would be conducive to bleed stream oxidation.

11.1 SYSTEM DESCRIPTION

The flow diagram for Runs 909-1A through 913-1A, operating with the trap-out funnel, is shown in Figure 11-1. This system was adapted from the two-scrub-

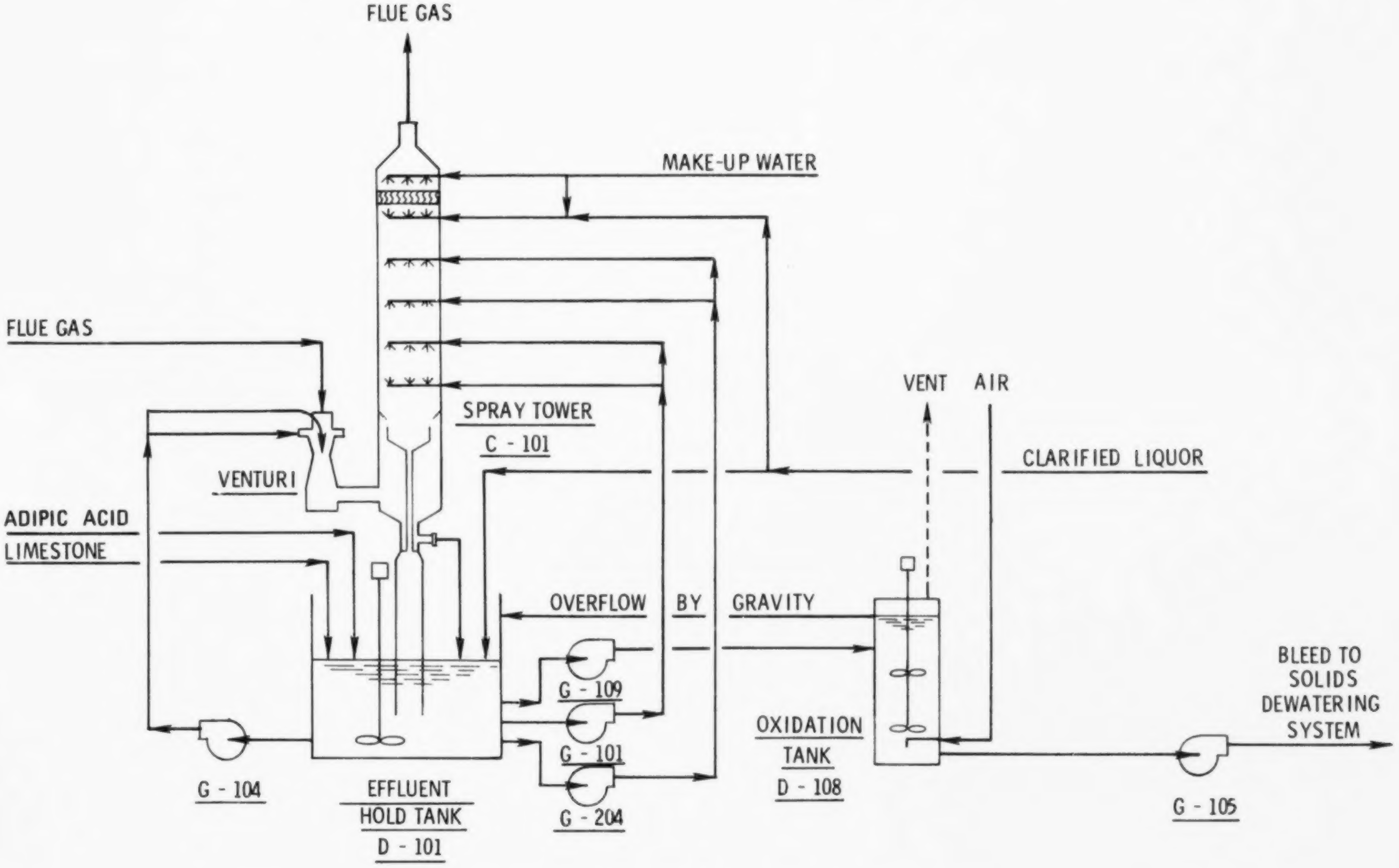

FLUE GAS
MAKE-UP WATER
FLUE GAS
SPRAY TOWER
C - 101
VENT
AIR
CLARIFIED LIQUOR
VENTURI
ADIPIC ACID
LIMESTONE
OVERFLOW BY GRAVITY
BLEED TO SOLIDS DEWATERING SYSTEM
G - 109
G - 101
G - 204
OXIDATION TANK
D - 108
G - 104
EFFLUENT HOLD TANK
D - 101
G - 105

Figure 11-1

Flow Diagram For Bleed Stream Oxidation In The Venturi/Spray Tower System With Trap-Out Funnel ber-loop forced oxidation configuration (Figure 4-1) by recirculating the venturi slurry to and from the same effluent hold tank for the spray tower. The system bleed stream was taken from the common effluent hold tank and sent to the oxidation tank. The arrangement of this oxidation tank (D-108) is shown in Figure 4-2 and described in Section 4-1.

For Runs 915-1A through 915-1C operating without the trap-out funnel, the flow configuration is depicted in Figure 11-2. The arrangement of the oxidation tank (D-208) is shown in Figure 9-2.

11.2 DISCUSSION OF TEST RESULTS

Table 11-1 gives the major test conditions and the average results for the five runs (Runs 909-1A through 913-1A) made at high pH and low adipic acid concentration. The results of the three runs (Runs 915-1A through 915-1C) conducted at low pH and high adipic acid concentration are summarized in Table 11-2.

11.2.1 Oxidation of Bleed Stream at High pH and Low Adipic Acid Concentration

Runs 909-1A through 913-1A (Table 11-1) were all made at a nominal adipic acid concentration of 1500 ppm. The limestone stoichiometry was controlled at 1.1 to 1.2 for these runs, resulting in a rather high scrubber inlet pH of 5.2 to 5.4 and an oxidation tank pH of 5.5 to 7.0. Controlled run conditions common to all of the tests were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Venturi slurry rate:	600 gpm

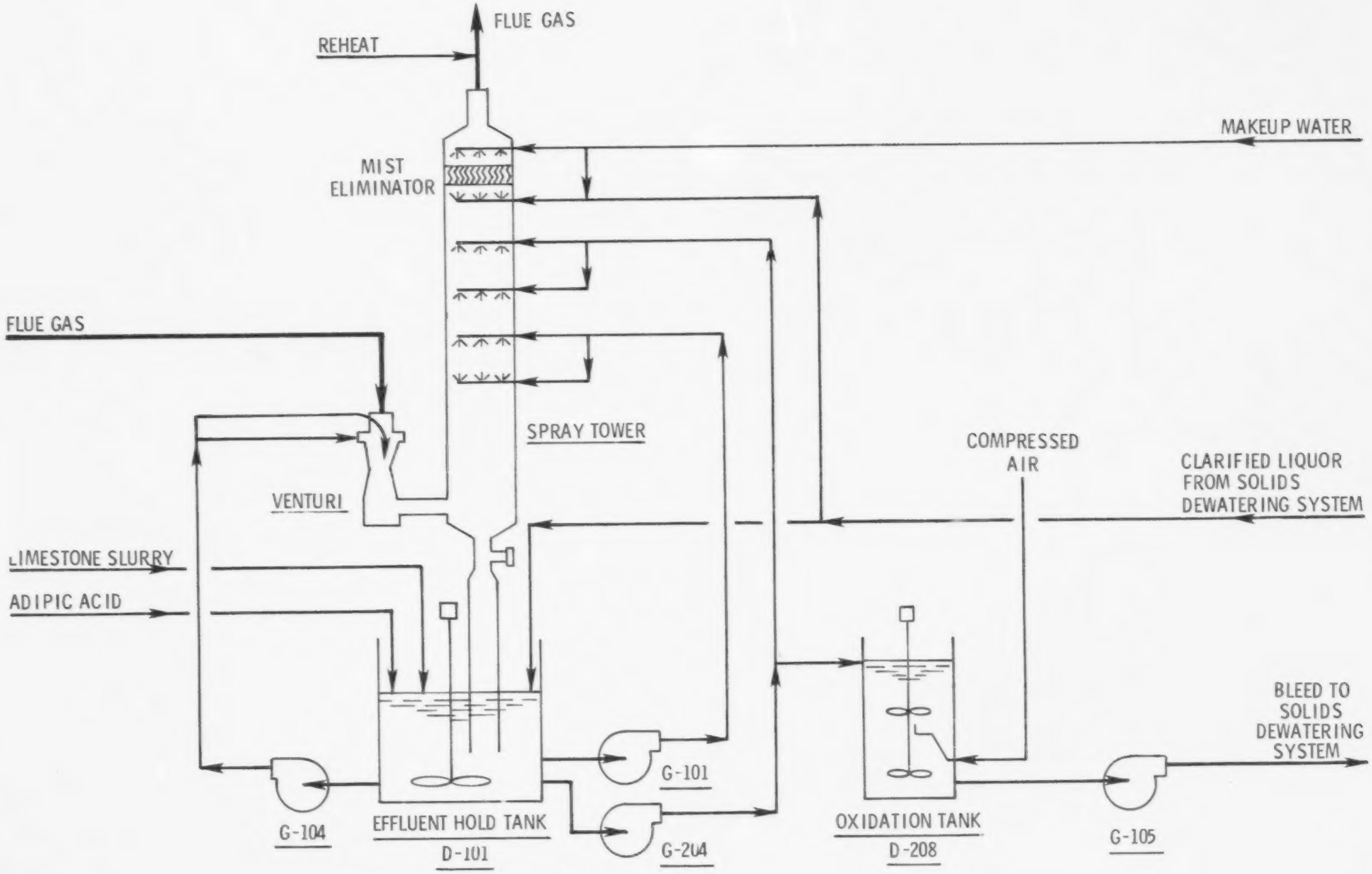

FLUE GAS
REHEAT
MAKEUP WATER
MIST
ELIMINATOR
FLUE GAS
SPRAY TOWER
COMPRESSED
AIR
CLARIFIED LIQUOR
FROM SOLIDS
DEWATERING SYSTEM
VENTURI
LIMESTONE SLURRY
ADIPIC ACID
BLEED TO
SOLIDS
DEWATERING
SYSTEM
G-101
G-104
EFFLUENT HOLD TANK
D-101
G-204
OXIDATION TANK
D-208
G-105

Figure 11-2

Flow Diagram For Bleed Stream Oxidation
In The Venturi/Spray Tower System Without Trap-Out Funnel

Table 11-1

RESULTS OF VENTURI/SPRAY TOWER BLEED STREAM OXIDATION TESTS AT HIGH pH AND LOW ADIPIC ACID CONCENTRATION

Major Test Conditions	909-1A	910-1A	911-1A	912-1A	913-1A
Fly ash loading	High	High	High	High	High
Gas rate, acfm @ 300^{o}F	18,000	35,000	35,000	35,000	18,000
Venturi liquor rate, gpm	600	600	600	600	600
Spray tower liquor rate, gpm	1600	1600	1600	1600	1600
Percent solids recirculated (controlled)	15	15	15	15	15
Residence times (min)/Tank level (ft): EHT	11.8/11	11.8/11	11.8/11	11.8/11	11.8/11
Oxidation Tank	/18	/18	/18	/18	/18
Limestone stoich. ratio (controlled)	1.2	1.1	1.1	1.1	1.1(1)
Adipic acid concentration, ppm	1500	1500	1500	1500	1500
Air rate to oxidizer, scfm	120	240	240	350	120
Venturi pressure drop, Inches H_2O	9	9	7.5	7.5	8.0
Recycle flow from oxidation tk to EHT, gpm	0	0	60	0	0
Run-Average Results					
Start-of-run date	3/30/79	4/11/79	4/16/79	4/24/79	4/26/79
Onstream hours	239	127	134	53	23
Percent SO_2 removal	96	95	95	96	98
Inlet SO_2 concentration, ppm	2825	2550	2400	2650	2350
Adipic acid concentration, ppm	1475	1500	1575	1500	1625
Scrubber percent solids recirculated	12.1	15.3	15.0	14.0	13.5
Scrubber inlet pH	5.30	5.25	5.30	5.40	5.20
Oxidation tank pH	5.6	7.0	5.6	7.0	5.5
Limestone utilization	94	96	85	93	96
Sulfite oxidation in oxidation tk, %	95	71	99	40	95
Sulfite oxidation in scrubber inlet, %	37	28	70	33	36
Gypsum sat'n in oxidation tank, %	90	85	95	95	95
Gypsum sat'n in scrubber inlet, %	105	100	100	100	105
Oxidation tk liquor $SO_3^=$ concentration, ppm	70	95	40	125	125
Air stoichiometry, lb-atoms O/lbmole SO_2 absorbed	1.50	1.75	1.85	2.40	1.75
Filter cake solids, wt %	84	75	84	63	79
Mist eliminator restriction, %	-	2	-	-	0

Note: (1) To insure low pH & high oxidation the pH was controlled at 5.0 with 4.9 underride.

Table 11-2

RESULTS OF VENTURI/SPRAY TOWER BLEED STREAM
OXIDATION TESTS AT LOW pH AND HIGH ADIPIC ACID CONCENTRATION

Major Test Conditions	915-1A	915-1B	915-1C
Fly ash loading	High	High	High
Flue gas rate, acfm @ 300°F	35,000	35,000	35,000
Venturi liquor rate, gpm	600	600	600
Spray tower liquor rate, gpm	1600	1600	1600
Percent solids recirculated (controlled)	15	15	15
EHT Res. time (min)/tank level (ft)	9.1/8.5	9.1/8.5	9.1/8.5
Oxid. Tk. Res. time (min)/tank level (ft)	-/17	-/17	-/17
Scrubber inlet pH (controlled)	5.1	5.1	4.8
Adipic acid concentration, ppm	4000	4000	4000
Air rate to oxidizer, scfm	200	300	200
Venturi pressure drop, inches H_2O	9	9	9
Run-Average Results			
Start-of-run-date	4/10/80	4/14/80	4/15/80
Onstream hours	98	24	127
Percent SO_2 removal	97.6	98.0	96.0
Inlet SO_2 concentration, ppm	2340	2550	2030
Adipic acid concentration, ppm	3840	4045	4140
Adipic acid consumption ratio, (actual/theor.)	3.33	5.20	1.26
Actual adipic acid consumption, lbs/ton SO_2 absorbed	40.1	44.5	15.4
Percent solids recirculated	15.2	15.5	15.6
Scrubber inlet pH	4.99	5.09	4.82
Oxidation tank pH	5.40	5.70	4.80
Limestone utilization, %	91	90	88
Sulfite oxidation in oxidation tank, %	69	73	98
Sulfite oxidation in scrubber inlet, %	26	25	54
Gypsum sat'n. in oxidation tank, %	105	105	100
Gypsum sat'n. in scrubber inlet, %	120	115	105
Oxidation tank liquor $SO_3^=$ concentration, ppm	115	95	140
Air stoich., lb atoms O/lb mole SO_2 absorbed	1.55	2.10	1.80
Centrifuge cake solids, wt%	70	79	79
Mist eliminator restriction, %	--	--	3

Spray tower slurry rate: 1600 gpm
Slurry solids concentration: 15 percent
Effluent hold tank residence time: 11.8 min.
Oxidation tank level: 18 ft
Adipic acid concentration: 1500 ppm

Run 909-1A. In the initial run, Run 909-1A, the flue gas rate was held at 18,000 acfm at 300°F, half the scrubber capacity. At this gas rate the bleed stream flow rate was about 15 gpm, compared to about 30 gpm normal bleed rate at full gas load. The oxidation tank residence time was therefore doubled to about 7.5 hours at 15 gpm, giving the bleed stream oxidation mode of operation the best chance of success. The results were encouraging. Although close attention was required to maintain the scrubber inlet pH at about 5.3, good control was achieved and oxidation of the bleed stream averaged 95 percent. Oxidation tank pH averaged 5.6. The air stoichiometry was 1.50 atoms oxygen/ mole SO_2 absorbed. Good SO_2 removal of 96 percent was attained at an inlet SO_2 concentration in the flue gas of 2825 ppm. The adipic acid concentration was 1475 ppm.

Run 910-1A. In Run 910-1A, the flue gas flow rate was increased to the full capacity of 35,000 acfm at 300°F. The corresponding bleed rate was about 30 gpm. The results showed that sufficiently low pH could not be held in the scrubber inlet slurry to give good oxidation without sacrificing SO_2 removal. Even during periods when the scrubber inlet pH averaged only 5.1, the oxidation tank pH was 6.9. The average scrubber inlet pH (effluent hold tank pH) was 5.25 which gave an average SO_2 removal of 95 percent at an inlet SO_2 concentration of 2550 ppm. With the inlet pH to the oxidation tank at 5.25, the oxidation tank pH averaged about 7.0 and oxidation dropped off to 71 percent even though the air stoichiometric ratio was up to 1.75 atoms oxygen/ mole SO_2 absorbed.

Run 911-1A. This run was made to see if a lower pH could be maintained in the oxidation tank by recycling 60 gpm of slurry back to the effluent hold tank (see Figure 11-1). It was believed that this would force more of the low pH liquor in the effluent hold tank through the oxidation tank. With a pH of 5.3 in the effluent hold tank, the oxidation tank pH was held at 5.6 and sulfite oxidation reached a high of 99 percent. Air stoichiometry was 1.85 atoms oxygen/ mole SO_2 absored. With 1575 ppm adipic acid in the liquor, the SO_2 removal averaged 95 percent at an inlet SO_2 concentration of 2400 ppm. Because of the 60 gpm recycle, limestone utilization was only 85 percent for Run 911-1A compared to 93 percent or higher for other runs. The recycle stream resulted in 70 percent oxidation in the scrubber slurry compared to 37 percent or less for other runs. The depletion of solid calcium sulfite crystal seeds in the scrubber slurry must have caused some degree of limestone blinding.

Run 912-1A. In Run 912-1A, the recirculation of liquor from the oxidation tank was stopped and the air rate was increased to the maximum in an attempt to oxidize the bleed without artificially lowering the oxidation tank pH by the recycle stream. The increased air rate only compounded the problems experienced in Run 910-1A. Although the oxidation tank pH was again 7.0, on the average, the oxidation dropped to 40 percent. The air stoichiometry was 2.40 atoms oxygen/mole SO_2 absorbed. The SO_2 removal, however, remained high at 96 percent with 2650 ppm SO_2 in the flue gas.

Run 913-1A. The purpose of Run 913-1A was to operate the system under the conditions of Run 909-1A (18,000 acfm gas rate at 300°F) when good oxidation had been achieved, to allow Radian Corporation to take adipic acid material balance samples around the oxidation tank. Good oxidation was again achieved with the lower bleed rate. At an average oxidation tank pH of 5.5, sulfite oxidation was 95 percent. The air stoichiometry was 1.75 atoms oxygen/mole SO_2 absorbed.

11.2.2 Oxidation of the Bleed Stream at Low pH and High Adipic Acid Concentration

Runs 915-1A through 915-1C (Table 11-2) were all made at a nominal adipic acid concentration of 4000 ppm. The scrubber inlet pH was controlled at 4.8 or 5.1 for these runs, resulting in a low oxidation tank pH of 4.8 to 5.7. Air rate to the oxidizer was also varied from 200 to 300 scfm for these runs. All other conditions were held constant. Oxidation tank slurry was not recycled back to the effluent hold tank in any of these tests. Full gas flow rate of 35,000 acfm was used in all three runs.

All tests achieved better than 95 percent SO_2 removal at 4.8 to 5.1 scrubber inlet pH and about 4000 ppm adipic acid. Average limestone utilizations were 88 to 91 percent.

However, good sulfite oxidation of 98 percent was achieved in only Run 915-1C when the scrubber inlet pH was controlled at 4.8 with an air stoichiometry of 1.80 atoms oxygen/mole SO_2 absorbed. Oxidation was only about 70 percent at 5.0 scrubber inlet pH and 1.55 air stoichiometry (Run 915-1A) or at 5.1 scrubber inlet pH and 2.10 air stoichiometry (Run 915-1B).

The oxidation tank pH was 5.4, 5.7, and 4.8 for Runs 915-1A, 915-1B, and 915-1C, respectively, as compared with 5.5 to 5.6 for Runs 909-1A, 911-1A, and 913-1A when good oxidation was achieved at 1.50 to 1.85 air stoichiometry. The poorer oxidation efficiency for Runs 915-1A, 915-1B, and 915-1C may be attributed to the poorer oxidizer arrangement shown in Figure 9-2.

11.2.3 Adipic Acid Consumption

Material balance calculations for Runs 915-1A through 915-1C showed that, under similar limestone utilizations of 88 to 91 percent, the actual-to-theoretical adipic acid consumption ratio increased from 1.26 to 5.20 when the scrubber inlet pH increased from 4.8 to 5.1, and the oxidation tank pH increased concurrently from 4.8 to 5.7. Actual adipic acid consumption increased correspondingly from 15.4 to 44.5 lb/ton SO_2 absorbed.

11.3 SUMMARY

The following is a summary of the test results:

- Bleed stream oxidation of limestone/adipic acid slurry is feasible if the oxidation tank pH can be maintained below about 6 with 1500 ppm of adipic acid acting as a pH buffer.
- Low oxidation tank pH can be accomplished by recycling the oxidation tank slurry (60 gpm) back to the effluent hold tank.
- The recycle between the oxidation tank and the effluent hold tank essentially creates an operating mode approaching that of forced oxidation within the scrubber loop.
- Bleed stream oxidation is also feasible without the recycle, but at a high oxidation tank residence time of about 7.5 hours based on the bleed stream flow rate of 15 gpm (at 18,000 acfm gas rate and 1500 ppm adipic acid).
- At 4.8 scrubber inlet pH and about 4000 ppm adipic acid concentration, 98 percent oxidation of sulfite was achieved in a less efficient oxidation tank with an air stoichiometry of 1.8 atoms oxygen/mole SO_2 absorbed. The oxidation tank pH was 4.8. The actual-to-theoretical adipic acid consumption ratio was only 1.26, corresponding to 21 percent unaccounted adipic acid loss. Actual adipic acid consumption was 15.4 lbs/ton SO_2 absorbed (8.7 lbs/ton limestone).

Section 12

SPRAY TOWER LIMESTONE/ADIPIC ACID LONG-TERM RELIABILITY TEST WITH ONE-SCRUBBER-LOOP AND TWO-TANK FORCED OXIDATION

A long-term reliability run, Run 917-1A, began on December 26, 1980, on the spray tower system (without the venturi) using adipic acid-enhanced limestone and two-tank forced-oxidation.

Unlike previous long-term tests, such as venturi/spray tower Runs 907-1A and 907-1B (see Section 4) and TCA Run 932-2A (see Section 13) in which operating conditions were not thoroughly optimized before the tests, Run 917-1A was made after several series of factorial tests (see Section 22). The test conditions selected for the run represented an optimum set based on the most recent knowledge with regard to pH, adipic acid consumption and concentration, limestone utilization, liquid-to-gas ratio, etc.

12.1 SYSTEM DESCRIPTION

The venturi scrubber was physically removed from Train 100 in June 1980, to allow operation with the spray tower alone. In August 1980, the spray tower external piping and the spray header assembly were modified to increase the maximum slurry flow capacity from 1600 to 2400 gpm.

Figure 12-1 shows the flow diagram for the long-term run, Run 917-1A, and reflects the modifications mentioned above.

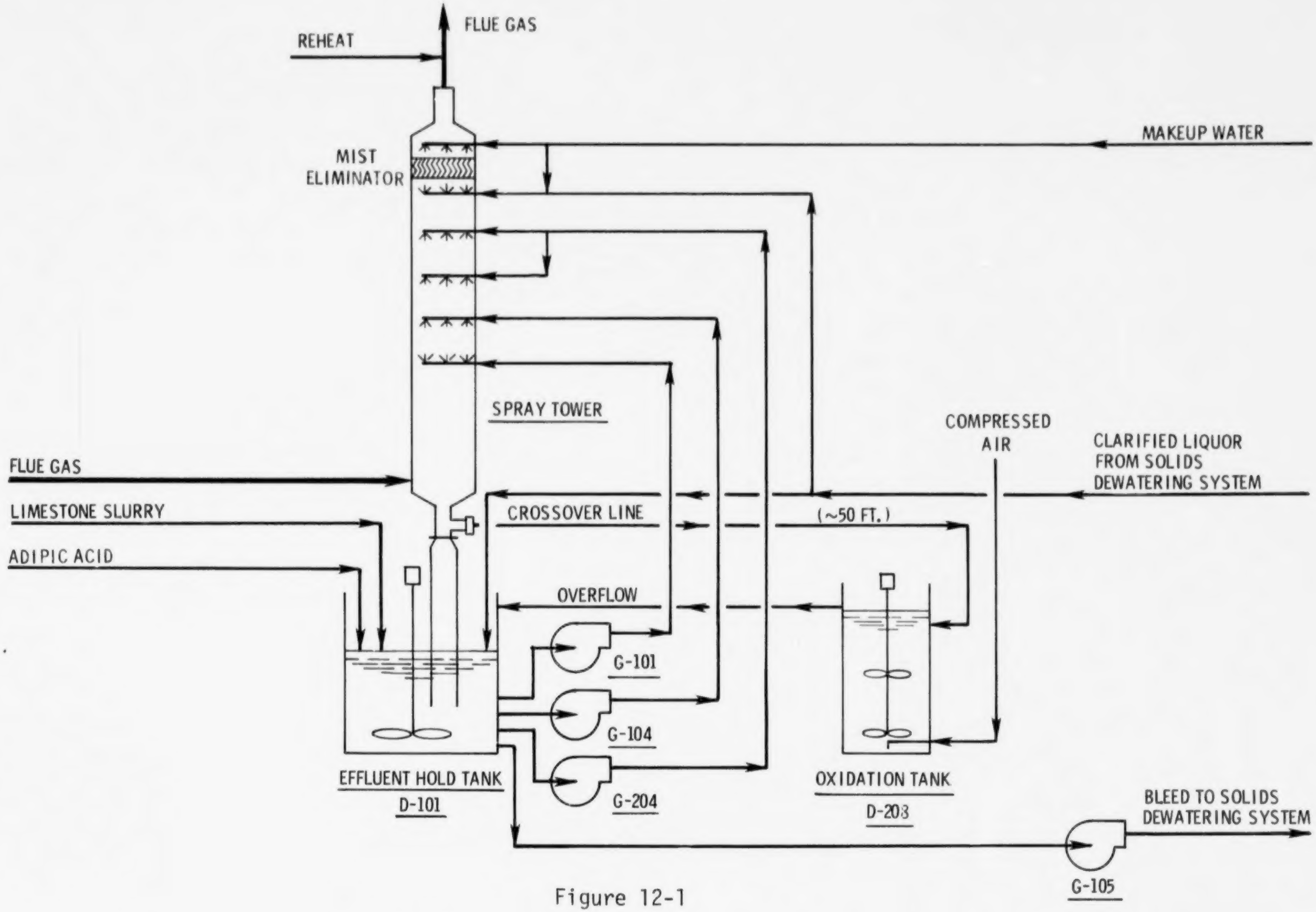

REHEAT
FLUE GAS
MIST ELIMINATOR
MAKEUP WATER
SPRAY TOWER
COMPRESSED AIR
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
FLUE GAS
LIMESTONE SLURRY
ADIPIC ACID
CROSSOVER LINE
(~50 FT.)
OVERFLOW
G-101
G-104
G-204
EFFLUENT HOLD TANK
D-101
OXIDATION TANK
D-203
BLEED TO SOLIDS DEWATERING SYSTEM
G-105

Figure 12-1

Spray Tower Only Configuration Using Two Tanks And Forced Oxidation

The oxidation tank (D-208) used in Run 917-1A was the same as that shown in Figure 9-2, except that the air injection point was moved down to a level below the lower turbine 3 inches from the bottom of the tank. Air was discharged downward through an open ell. With two-tank operation, there was no pump cavitation problem due to air-binding.

12.2 TEST OBJECTIVES AND JUSTIFICATIONS OF SELECTED TEST CONDITIONS

The prime objectives of Run 917-1A were to demonstrate the spray tower long-term (greater than one month) operating reliability with respect to scaling and plugging, and to maintain 90 percent or higher SO_2 removal at a changing flue gas flow rate which followed a typical daily boiler load cycle.

Major operating conditions selected for Run 917-1A and the justifications are presented below.

Fly ash loading. Flue gas with high fly ash loading (2 to 7 grains/dscf) was used to give a more severe test environment with regard to plugging and erosion.

Gas Flow Rate. To simulate a typical boiler load variation, flue gas flow rate was changed six times a day according to the following cycle:

Time of Change (at start of run)	Time of Change (beginning 1/9/81)	Gas Rate Changed To, acfm @ 300°F
0100	2300	20,000
0500	0300	30,000
0700	0500	35,000
1100	0900	30,000
1700	1500	35,000
2300	2100	30,000

To avoid changing the gas rate at the time of the operator shift change, the gas rate time schedule was advanced by one hour beginning December 31, 1980. It was advanced once again by one hour beginning January 9, 1981, to accommodate the particulate sampling schedule during the day shift.

Slurry flow rate. A constant 2400 gpm (600 gpm/spray header) slurry flow rate was selected to give a reasonable L/G value of 85 gal/mcf at the maximum gas rate of 35,000 acfm (at 300°F) for the desired 90 percent or higher SO_2 removal. In a full-scale plant, the slurry flow rate is usually maintained constant by using constant speed pumps. The maximum L/G was 150 gal/mcf at 20,000 acfm (at 300°F) gas rate and 2400 gpm slurry flow rate. With an 18-ft level in the oxidation tank and an 8.5-ft level in the effluent hold tank, the 2400 gpm slurry flow rate resulted in 2.8 minutes and 8.3 minutes residence times, respectively.

The L/G values of 85 to 150 gal/mcf were higher than those for Runs 916-1A through 916-1H in which limestone blinding was encountered in the scrubber effluent line (see Section 10). The higher L/G for Run 917-1A should give lower SO_2 make-per-pass and, therefore, reduce limestone blinding tendency in the effluent line.

Scrubber inlet pH and adipic acid concentration. An optimum scrubber inlet pH of 5.0 was selected based on the past Shawnee experience with adipic acid-enhanced limestone scrubbing. At lower pH, the SO_2 removal is sensitive to the variations in pH and inlet SO_2 concentration because of the reduced buffering activity of adipate and other alkaline species. On the other hand, higher pH increases the degradation and consumption of adipic acid and decreases the limestone utilization. With forced oxidation, higher pH also increases the potential of limestone blinding and reduces the oxidation efficiency (demanding higher air stoichiometry).

At the selected scrubber inlet pH of 5.0, the required adipic acid concentration was estimated to be 1300 ppm to achieve the desired 90 percent or higher SO_2 removal efficiency. Under these conditions and at the minimum L/G of 85 gal/mcf (the worst case), the predicted SO_2 removal is 92 percent with 2380 to 3090 ppm inlet SO_2 concentration (see Section 22).

Two-tank operation with forced oxidation. Forced oxidation produces predominantly gypsum waste sludge which has dewatering and handling characteristics superior to unoxidized sludge. Two-tank configuration, with forced oxidation in the first tank and limestone addition to the second, offers a number of advantages, as delineated in Section 10.

Air flow rate. A constant air rate to the oxidation tank of 200 scfm was chosen. This would give an adequate air stoichiometric ratio of at least 1.3 atom oxygen/mole SO_2 absorbed under the worst case conditions (maximum gas rate).

Recirculated slurry solids concentration. Slurry solids concentration was controlled at 15 percent by weight. Higher solids concentration causes a higher equipment erosion rate and higher mist eliminator fouling potential. On the other hand, low solids concentration gives an inadequate amount of solid crystal seeds and suspended limestone particles.

Solids dewatering equipment. A clarifier and rotary drum vacuum filter in series were used to provide the tightest possible liquor loop operation. This minimized the adipic acid consumption while providing a severe test environment of high dissolved solids concentration and high scaling tendency.

12.3 DISCUSSION OF TEST RESULTS

Run 917-1A started on December 26, 1980, and terminated on March 13, 1981, for a total of 1688 onstream hours (70 days). Steady-state operation was not reached until December 29, 1980, because of problems with the slurry recirculation pump (G-204) which supplied the slurry to the top two spray headers. Table 12-1 presents the average results of steady-state operation for Run 917-1A.

The overall results of the run were as good as expected. At 2660 ppm average inlet SO_2 concentration, SO_2 removal for the entire run varied within the extreme range of 87 to 99 percent at an L/G range of 85 to 150 gal/mcf. The overall run-average SO_2 removal was 93.4 percent. The daily (0000-2400 hours) average SO_2 removal ranged from 92 to 95 percent for the entire run.

During the first month of the test in January 1980, SO_2 removal gradually deteriorated at a controlled adipic acid concentration of 1300 ppm and a scrubber inlet pH of 5.0. At the minimum L/G of 85 gal/mcf (maximum gas rate of 35,000 acfm at 300°F), SO_2 removal sometimes dropped to below 90 percent and to as low as 87 percent. At the maximum L/G of 150 gal/mcf (20,000 acfm at 300°F), the removal was 97 to 99 percent. It should be emphasized, however, that the daily average SO_2 removal was never below 90 percent and stayed at 92 percent or higher during this period.

In order to maintain the SO_2 removal at 90 percent or higher at all times, the scrubber inlet pH was raised from 5.0 to 5.1 on January 30. The increase in pH was purposefully kept small because higher pH increases the consumption and degradation of adipic acid and decreases the limestone utilization. Since SO_2 removal is fairly sensitive to pH variations at these pH levels, it was expected that a small change in pH (from 5.0 to 5.1) would give the desired SO_2

Table 12-1

RESULTS OF SPRAY TOWER LONG-TERM RELIABILITY LIMESTONE RUN 917-1A WITH ADIPIC ACID ADDITION AND TWO-TANK FORCED OXIDATION

Major Test Conditions	917-1A
Fly ash loading	High
Gas rate, acfm @ 300°F	20,000-35,000 (1)
Slurry rate, gpm	2400
Slurry solids concentration, wt% (controlled)	15
Inlet liquor pH (controlled)	5.0/5.1 (2)
Adipic acid addition point	Effluent hold tank
Adipic acid concentration, ppm	(3)
Oxidation tank residence time, min/tank level, ft	2.8/18
EHT residence time, min/tank level, ft	8.3/8.5
Dewatering system	Clarifier/drum or belt filter
Air rate to oxidation tank, scfm	200
Run-Average Results	
Start-of-run date	12/26/80
Onstream hours	1688 (4)
Percent SO_2 removal	87-99
Inlet SO_2 concentration, ppm	2660
Adipic acid concentration, ppm	1350/1740 (5)
Adipic acid consumption, lbs/ton of SO_2 absorbed	9.3/8.9 (5)
Adipic acid consumption ratio (actual/theoretical)	4.7/3.2 (5)
Slurry solids concentration, wt%	15.2
Scrubber inlet liquor pH	5.0/5.1 (6)
Scrubber outlet liquor pH	4.7
SO_2 make-per-pass, m-moles/liter	4.0-8.9
Limestone utilization, %	92.6
Scrubber inlet liquor sulfite concentration, ppm	36
Scrubber outlet liquor sulfite concentration, ppm	440
Sulfite oxidation, %	99.8
Filter cake solids, wt%	86
Scrubber inlet liquor gypsum saturation, %	93
Air stoich., atoms O/mole SO_2 absorbed	1.4-2.4
Mist eliminator restriction, %	0

Notes:

(1) Gas rate was varied in accordance with a "typical" daily boiler load cycle.

(2) Changed to 5.1 from 5.0 on 1/30/81. Changed back to 5.0 on 3/10/81.

(3) Changed to 1700 ppm from 1300 ppm on 2/6/81.

(4) Total hours include 76 hours of unsteady-state operation from 12/26 to 12/29/80.

(5) First value before 2/6/81 and second value beginning 2/6/81.

(6) Average 5.0 pH before 1/30/81 and 5.1 beginning 1/30/81.

removal improvement by 1 or 2 percentage points. However, no appreciable effect of this change was noted and the deterioration of SO_2 removal continued.

In the meantime, it was noticed that the rate at which adipic acid was added to the system to maintain the desired 1300 ppm concentration had been decreasing significantly. For example, the average adipic acid feed rate was about 80 lb/day from December 29 to January 12. This dropped to 52 lb/day from January 13 to January 25, and further to about 44 lb/day from January 26 to February 6. It was hypothesized that some organic acids, which are either ineffective or less effective in enhancing SO_2 removal, had been accumulating in the scrubber liquor. These "background" acids are believed to be either the adipic acid decomposition products or introduced into the system through flue gas and fly ash. These acids are undoubtedly detectable by the silicic acid absorption procedure used at Shawnee for adipic acid determination (see Appendix N).

Indirect evidence pointing to the accumulation of the "background" acids was the simultaneous increase in chloride concentration from about 1500 to 2500 ppm during these times with a very tight liquor loop (87 percent filter cake solids).

Consequently, the adipic acid concentration was raised from 1300 to 1700 ppm on February 6 (at 985 onstream hours) to compensate for the effect of the "background" acids. With 1700 ppm adipic acid, SO_2 removal improved from 87-92 percent to 90-93 percent at the minimum L/G of 85 gal/mcf, and stayed at 90 percent or higher at all times.

The ranges of SO_2 removal at various L/G ratios (constant slurry flow rate of 2400 gpm) are summarized below:

L/G, gal/mcf	Gas Rate,* acfm @ 300°F	Percent SO_2 Removal
85	35,000	87-92 (1300 ppm adipic acid) 90-93 (1700 ppm adipic acid)
100	30,000	92-95
150	20,000	97-99

*Daily average gas rate = 30,400 acfm

Sulfite oxidation was excellent throughout the run and averaged 99.8 percent. Limestone utilization averaged 92.6 percent. Average filter cake solids concentration was 86 percent and the scrubber inlet liquor gypsum saturation was 93 percent.

The consumption rate of adipic acid at 1350 ppm average concentration (before February 6, 1981) was 9.3 lb/ton SO_2 absorbed or 5.5 lb/ton of limestone, which was 4.7 times the theoretical requirement. At 1740 ppm average concentration (beginning February 6, 1981), the consumption rate was 8.9 lb/ton SO_2 absorbed or 5.3 lb/ton of limestone, corresponding to 3.2 times the theoretical requirement. The following table gives a breakdown of the adipic acid addition rates:

Run 917-1A Adipic Acid Consumption

	At 1350 ppm (before 2/6/81)		At 1740 ppm (beginning 2/6/81)	
	lb/hr	lb/ton limestone feed	lb/hr	lb/ton limestone feed
Discharged with filter cake	0.51	1.2	0.74	1.6
Unaccounted	1.90	4.3	1.66	3.7
Total	2.41	5.5	2.40	5.3

During Run 917-1A, the scrubber system was shut down 10 times, including four times due to power plant-related outages. Table 12-2 summarizes the cause and and duration of each shutdown.

Table 12-2

SYSTEM SHUTDOWNS DURING RUN 917-1A

Date	Downtime, Hours	Cause for Shutdown
1/13/81	5 1/4	I.D. fan damper problem, unable to control low flue gas flow
1/21/81*	20 1/2	Unit 10 transformer problem
2/6/81	2 3/4	Inspection
2/10/81	2 3/4	I.D. fan damper problem, unable to control low flue gas flow
2/24/81	11 1/2	Inspection and rebuilt G-204 slurry pump
2/26/81	9 1/4	Oxidation air compressor problem
2/27/81*	58	Plant water line leakage
3/3/81	46 1/4	Replaced I.D. fan motor coupling and bearings, high fan vibration
3/11/81*	1 3/4	"A" side air preheater oil pump coupling problem
3/12/81*	3 1/2	"A" side air preheater oil pump coupling problem

* Power plant-related outages.

Power plant-related outages = 84 hours
Scrubber system-related outages = 78 hours
Total = 162 hours

Total onstream hours = 1688

Onstream factor = 1688/(1688 + 78) = 95.6%

The power plant-related outages totaled 84 hours. The scrubber system problems caused 78 hours of total downtime. Excluding the power plant-related outages, the scrubber onstream factor was 95.6 percent. It should be noted that the majority of scrubber-related shutdowns were caused by mechanical problems.

Inspections of the spray tower internals during the shutdowns and at the end of the run showed that there was no scaling or plugging inside the tower other than occasional plugging of the slurry spray nozzles. The mist eliminator was essentially clean throughout the run, with only some slurry dust on the chevron blades which is typical of slurry operation.

12.4 SUMMARY

Successful operation of the spray tower with adipic acid-enhanced limestone and with two-tank forced oxidation was demonstrated in a long-term run lasting 1688 onstream hours with an onstream factor of 95.6 percent.

Daily average SO_2 removal for the run varied between 92 and 95 percent with a run-average removal of 93.4 percent. Average inlet SO_2 concentration was 2660 ppm. Liquid-to-gas ratio varied between 85 and 150 gal/mcf (20,000 to 35,000 acfm gas rate at 300°F with constant 2400 gpm slurry flow rate). Limestone utilization averaged 92.6 percent and the filter cake solids averaged 86 percent. Sulfite oxidation was excellent at 99.8 percent. Adipic acid consumption was about 9 lb/ton SO_2 absorbed (5.4 lb/ton limestone), which was about 4 times the theoretical requirement.

12.5 RECOMMENDATIONS

Based on the results of Run 917-1A, the following design conditions can be recommended for a spray tower operating with adipic acid enhanced-limestone and with two-tank forced oxidation for 90 percent or higher SO_2 removal (2660 ppm inlet SO_2 concentration):

Superficial gas velocity = 9.4 ft/sec (35,000 acfm @ 300°F at Shawnee)
Minimum L/G = 85 gal/mcf (4 spray headers @ 4 ft spacing)
Slurry solids concentration = 15 percent (including fly ash)
Spray tower inlet pH = 5.0
Minimum adipic acid concentration = 1700 ppm
Minimum oxidation tank level = 18 ft
Minimum oxidation tank residence time = 2.8 minutes
Effluent hold tank residence time = 8 minutes
Minimum air stoichiometry = 1.4 atoms oxygen/mole SO_2 absorbed

These conditions are required for reliable, efficient spray tower operation at maximum load, at least in the case of Shawnee spray tower using Fredonia limestone (see Appendix C.2).

Section 13

TCA LIMESTONE/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND WITHOUT FORCED-OXIDATION

Testing with adipic acid on the TCA lime and limestone systems began in July 1978. Initial tests were conducted without forced oxidation. SO_2 removal as high as 96 percent was achieved in the limestone system with up to 1500 ppm of adipic acid, and up to 97.5 percent removal in the lime system with up to 1200 ppm adipic acid. Results of these adipic acid-enhanced tests without forced oxidation are reported in this section for limestone and in Section 14 for lime.

13.1 SYSTEM DESCRIPTION

The TCA was operated in a single-loop scrubbing configuration as shown in Figure 13-1. The TCA contained three beds of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres retained between four bar grids. Each bed contained 5 inches static height of spheres.

The effluent hold tank was 7 ft in diameter and operated at a 17-ft slurry level giving a 4.1 minute residence time at the slurry recirculation rate of 1200 gpm. Limestone and adipic acid were added directly to the effluent hold tank.

The dewatering system consisted of a clarifier followed by a solid bowl centrifuge. All clarified liquor from the dewatering system was returned to the scrubber loop either via the effluent hold tank or the mist eliminator underside sprays.

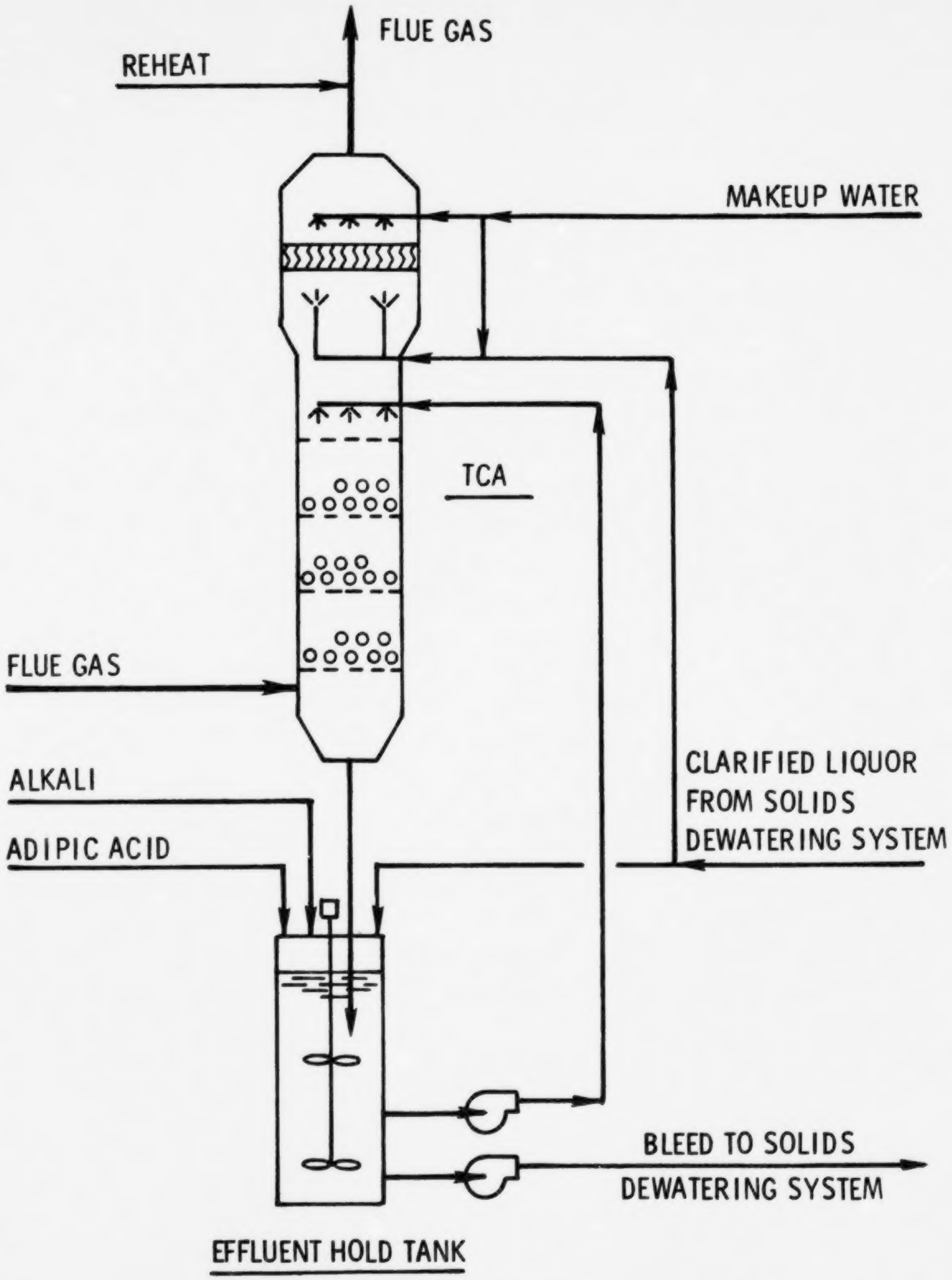

FLUE GAS
REHEAT
MAKEUP WATER
TCA
FLUE GAS
CLARIFIED LIQUOR
FROM SOLIDS
DEWATERING SYSTEM
ALKALI
ADIPIC ACID
BLEED TO SOLIDS
DEWATERING SYSTEM
EFFLUENT HOLD TANK

Figure 13-1

Flow Diagram For Adipic Acid-Enhanced Scrubbing In The TCA System Without Forced Oxidation

13.2 DISCUSSION OF TEST RESULTS

Beginning in July 1978, a series of 8 limestone tests was conducted on the TCA system to demonstrate the effects of adipic acid on enhancing SO_2 removal in a system without forced oxidation. Results of these tests are summarized in Table 13-1. Unless otherwise specified, controlled run conditions common to all of the tests were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Flue gas rate:	30,000 acfm at 300°F
Slurry flow rate:	1200 gpm (50 gal/mcf)
Slurry solids concentration:	15 percent

13.2.1 Effect of Adipic Acid Concentration

TCA limestone Runs 926-2A through 929-2A were made under identical conditions except for adipic acid concentration. In these runs limestone stoichiometry was controlled at 1.2 moles Ca/mole SO_2 absorbed. The effect of adipic acid on SO_2 removal was:

TCA Run	Actual Adipic Acid Conc., ppm	Percent SO_2 Removal
926-2A	0	71
927-2A	350	75
929-2A	885	92
928-2A	1600	93

SO_2 removal increased from 71 percent with no adipic acid to 92 percent with 885 ppm in the slurry liquor. Increasing adipic acid further to 1600 ppm increased SO_2 removal only slightly to 93 percent. Thus, the majority of the adipic acid-enhancement was achieved in the TCA at a concentration somewhere between 350 and 885 ppm.

Table 13-1

RESULTS OF ONE-SCRUBBER-LOOP TCA LIMESTONE/ADIPIC ACID TESTS WITHOUT FORCED OXIDATION

Major Test Conditions(1)	926-2A	927-2A	928-2A	929-2A	930-2A	931-2A	932-2A(2)	933-2A(3)
Fly ash loading	High	High	High	High	High	High	High	High
Adipic acid concentration, ppm	0	300	1500	750	750	750	1500	0
Gas rate, acfm @ 300^{o}F	30,000	30,000	30,000	30,000	30,000	30,000	20,000-30,000	30,000
Slurry rate, gpm	1200	1200	1200	1200	1200	1200	1200	1200
Slurry solids concentration, wt %	15	15	15	15	15	15	15	15
LS stoichiometric ratio controlled at	1.2	1.2	1.2	1.2	1.35	1.05	1.2	1.2
EHT residence time, min.	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
EHT level, ft	17	17	17	17	17	17	17	17
Run Average Results								
Start-of-Run Date	7/4/78	8/4/78	8/22/78	9/5/78	9/13/78	9/20/78	9/26/78	1/25/79
Onstream hours	192	374	252	186	162	137	833	328
SO_2 removal, %	71	75	93	92	93	77	96	76
Inlet SO_2 concentration, ppm	2750	2300	2600	2300	2550	2300	2450	1950
SO_2 make-per-pass, m-moles/liter	10.1	9.1	12.8	11.2	12.6	9.4	4-18	7.9
TCA inlet liquor gypsum saturation, %	90	110	100	110	80	110	110	110
Sulfite oxidation, %	13	19	14	10	13	24	21	24
Limestone utilization, %	80	84	85	80	75	93	82	83
TCA inlet pH	5.65	5.30	5.40	5.50	5.60	4.95	5.30	5.45
Adipic acid concentration, ppm	0	350	1600	885	700	840	1620	0
Centrifuge solids, wt %	37(4)	62	59	59	58	62	61	57
Mist eliminator restriction, %	1	3	0	0	0	0	0	0

Notes:
(1) All runs were made with 3 beds and 5 inches per bed of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres.
(2) Long-term realibility test.
(3) Bioassay sampling test.
(4) Clarifier only.

13.2.2 Effect of Limestone Stoichiometry and pH

Limestone stoichiometry was explored at a nominal adipic acid concentration of 750 ppm and a liquid-to-gas ratio of 50 gal/mcf with the following results:

TCA Run	Limestone Stoichiometry mole Ca/mole SO_2 absorbed	TCA Inlet pH	Percent SO_2 Removal
931-2A	1.05	4.9	77
929-2A	1.20	5.5	92
930-2A	1.35	5.6	93

Thus, it is apparent that the system required a limestone stoichiometry of only about 1.2 to maintain sufficiently high pH to achieve the full SO_2 removal enhancement with adipic acid. Additional limestone did not significantly increase SO_2 removal.

13.2.3 TCA Demonstration Run 932-2A

Run 932-2A, a month-long demonstration run, was made with adipic acid-enhanced limestone slurry to demonstrate both operational reliability with respect to scaling and plugging and the removal enhancement capability of the adipic acid additive.

The run began on September 26, 1978 and terminated on November 2, 1978 for a total of 833 onstream hours (35 days). During the run, the scrubber was out of service for 48 hours due to a boiler outage caused by a tube leak, 5 hours for a scheduled inspection, and 8 hours for unscheduled outages to clean and repair the scrubber I.D. fan damper.

Excluding boiler outages and scheduled inspections, Run 932-2A operated with an onstream factor of 99.0 percent.

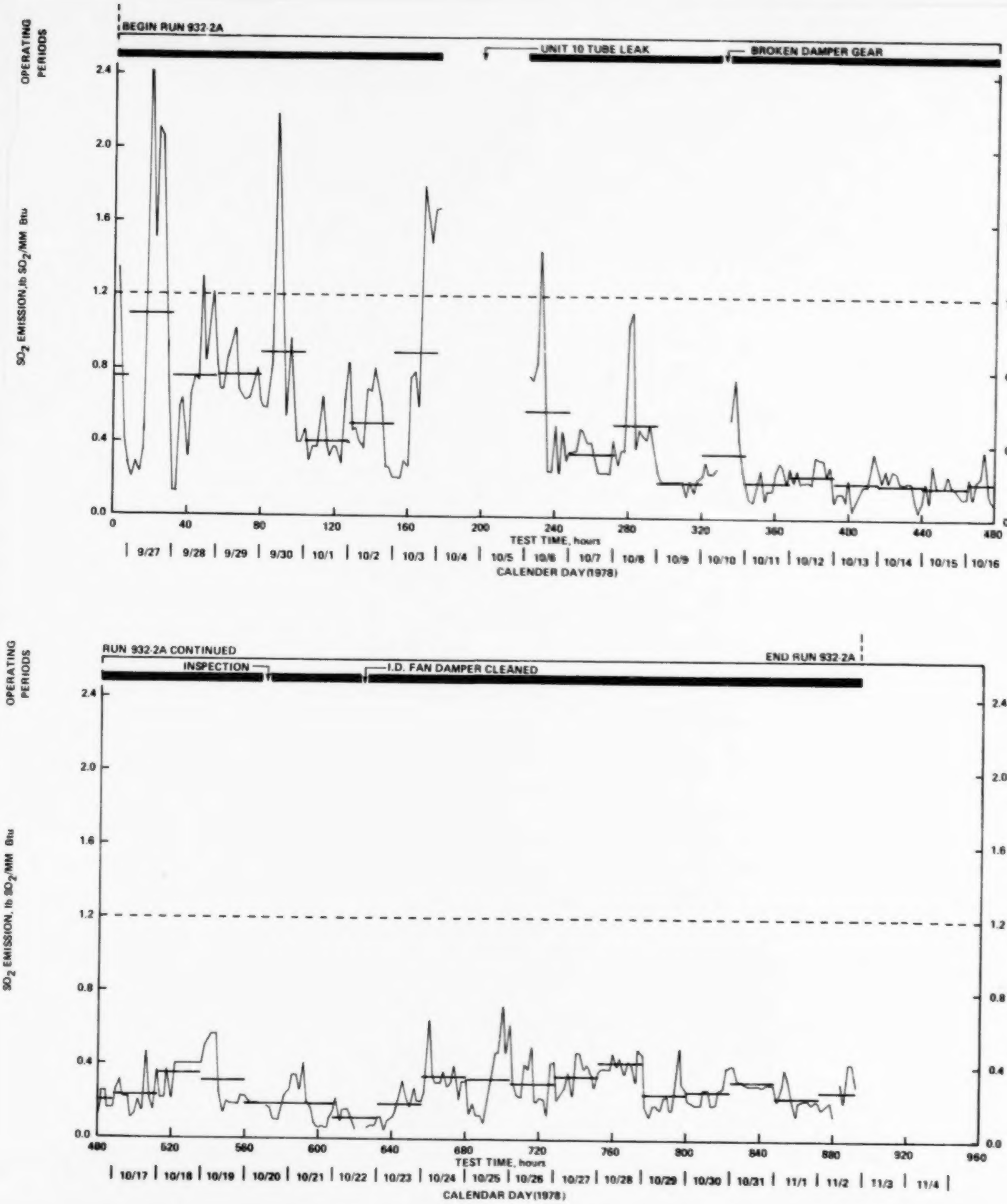
The run was controlled at a nominal 1.2 limestone stoichiometric ratio and 1500 ppm adipic acid concentration in the slurry liquor. Slurry solids concentration was controlled at 15 percent. The flue gas flow rate was varied between 20,000 and 30,000 acfm (8.4 to 12.5 ft/sec superficial gas velocity) as the boiler load fluctuated between 100 and 150 MW. The slurry recirculation rate was fixed at 1200 gpm (L/G = 50 to 75 gal/mcf). As with all runs during this test block, the effluent hold tank residence time was only 4.1 minutes.

SO_2 removal during the run averaged 96 percent at an average inlet SO_2 concentration of 2450 ppm. Excluding the first few days of unsteady-state operation, SO_2 removal stayed within the narrow range of 94 to 98 percent as the inlet SO_2 concentration varied widely between 1400 and 3500 ppm.

SO_2 emissions were calculated for Run 932-2A on the same basis as for the venturi/spray tower Runs 907-1A and 907-1B (see Section 4). Figure 13-2 shows the calculated SO_2 emissions for the TCA run. Average SO_2 emissions for each 24-hour period (0000-2400 hours) are indicated by horizontal lines on the figure.

During the first seven days (September 26 through October 3), SO_2 emissions were relatively high and widely varying. The highest daily average emissions were 1.1 lb $SO_2/10^6$ Btu on September 27 and 0.9 lb $SO_2/10^6$ Btu on both September 30 and October 3.

The relatively high SO_2 emissions resulted from frequent excursions to low pH in the scrubber inlet slurry liquor as the test personnel were trying to control the limestone stoichiometric ratio at 1.2 with widely varying inlet SO_2 concentrations (1000 to 3500 ppm). Beginning on October 6 after the boiler outage, a scrubber inlet pH underride of 5.1 was implemented in addition to the limestone stoichiometric ratio control value of 1.2. This combined stoichiometry/pH control produced the improved results shown for the remainder of the run.



Note: Horizontal bars indicate 24-hr (midnight-to-midnight) run averages

Figure 13-2. SO_2 Emissions During TCA Run 932-2A

SO_2 emissions for the 27-day period from October 6 through the end of the run on November 2 averaged only 0.26 lb/10^6 Btu. The highest 24-hour average SO_2 emission during this period was only 0.44 lb/MM Btu.

The mist eliminator was completely clean at the end of the run and the entire scrubber system was free of scaling and plugging.

Limestone utilization during the run averaged 82 percent. Discharge solids from the centrifuge averaged about 61 percent which is typical of unoxidized limestone sludge.

In summary, the objectives of this run were met. High removal was consistently achieved at a good limestone utilization and no fouling, scaling, or plugging occurred.

13.2.4 Adipic Acid Consumption

As with the forced oxidation runs on the venturi/spray tower system (see Section 4.2.7), adipic acid consumption in these initial TCA runs was greater than anticipated. An adipic acid material balance calculation was made during Run 932-2A between October 10 and October 30, 1978, a total of 21 days:

Run 932-2A Adipic Acid Consumption

	lb/hr	lb/ton limestone feed
Discharged with centrifuge cake	1.9	4.2
Unaccounted	2.2	5.0
Total	4.1	9.2

As already discussed in Section 4.2.7, the unaccounted loss in this run without forced oxidation of 2.2 lb/hr compares with 2.9 lb/hr for venturi/spray tower

Run 907-1B with forced oxidation. Thus, it appears that air sparging for forced oxidation increases adipic acid losses.

13.2.5 Bioassay Sampling Test

Run 933-2A was made to provide base case flue gas and slurry samples, from the TCA limestone scrubbing system without adipic acid and without forced oxidation, for Level 1 bioassay analyses.

These samples have been tested by Litton Bionetics, Inc. and Battelle Columbus Laboratories and compared with samples taken for venturi/spray tower Run 908-1A (see Section 4.2.8) which was made with adipic acid-enhanced limestone and forced oxidation (References 18 and 19).

Run 933-2A was made under the same conditions as Run 926-2A. An increase in SO_2 removal (71 to 76 percent) was experienced during Run 933-2A, due mainly to decreased inlet SO_2 concentration (2750 to 1950 ppm). Other test results are similar for the two runs.

13.3 SUMMARY

The following is a summary of the test results and findings:

- At a limestone stoichiometric ratio of 1.2, corresponding to 5.3-5.65 scrubber inlet pH at 4.1 minutes residence time, the majority of the adipic acid-enhancement was achieved in the TCA at a concentration somewhere between 350 and 885 ppm.
- Full enhancement of SO_2 removal with adipic acid required only about 1.2 limestone stoichiometry or a scrubber inlet pH greater than about 5.2. Higher limestone stoichiometry did not significantly increase SO_2 removal.

- Reliable operation of the TCA without forced oxidation was demonstrated in a 833-hour run. SO_2 removals consistently higher than 94 percent and averaging 96 percent were achieved with 1620 ppm adipic acid and 82 percent limestone utilization (5.3 average scrubber inlet pH). The effluent hold tank residence time was only 4.1 minutes.

Section 14

TCA LIME/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND WITHOUT FORCED-OXIDATION

Although emphasis at Shawnee was on adipic acid enhancement in the limestone system because of its economic advantage, testing was conducted on the TCA to demonstrate that adipic acid is also effective with lime.

A total of 7 runs were made on the TCA system without forced oxidation, 3 runs (Runs 976-2A, 976-2B, and 977-2A) in July 1978 and 4 runs (Runs 978-2A through 981-2A) in February and March 1979. The flow configuration for these runs is given in Figure 13-1. The test results are summarized in Table 14-1.

14.1 DISCUSSION OF TEST RESULTS

Runs 976-2A, 976-2B, and 977-2A were made with fresh lime added to the scrubber downcomer, whereas Runs 978-2A through 981-2A were made with lime added to the effluent hold tank. (Previous tests had indicated that addition of lime to the downcomer reduces gypsum saturation in the liquor.) All runs were conducted using flue gas with high fly ash loading (2-7 grains/dry scf), 30,000 acfm (@ 300°F) gas rate, a scrubber inlet pH of 7.0, and a 17-ft slurry level in the effluent hold tank. Run 976-2A was made inadvertently with a high slurry solids concentration of 15 percent as opposed to the desired 8 percent, used for the remaining runs. Shawnee lime tests were usually conducted with 8 percent slurry solids concentration (including fly ash), as compared to 15 percent solids (including fly ash) normally used for limestone tests. These concentrations are

Table 14-1

RESULTS OF ONE-SCRUBBER-LOOP TCA LIME/ADIPIC ACID TESTS WITHOUT FORCED OXIDATION

Major Test Conditions[1]	976-2A	976-2B	977-2A	978-2A	979-2A	980-2A	981-2A
Fly ash loading	High	High	High	High	High	High	High
Adipic acid concentration, ppm	0	0	300	0	600	1200	1200
Gas Rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Slurry rate, gpm	1200	1200	1200	1200	1200	1200	900
Slurry solids concentration, wt %	15	8	8	8	8	8	8
TCA inlet pH controlled at	7.0	7.0	7.0	7.0	7.0	7.0	7.0
EHT residence time, min.	4.1	4.1	4.1	4.1	4.1	4.1	5.4
EHT level, ft	17	17	17	17	17	17	17
Lime addition point[2]	DC	DC	DC	EHT	EHT	EHT	EHT
Run-Average Results							
Start-of-run date	7/12/78	7/19/78	7/25/78	2/8/79	2/13/79	2/22/79	3/12/79
Onstream hours	160	133	236	116	177	247	70
Percent SO_2 removal	70	67	80	83	93	97.5	92
Inlet SO_2 concentration, ppm	2850	2950	2700	2350	2900	2750	2600
SO_2 make-per-pass, m-moles/l	10.5	10.7	11.6	10.3	14.3	14.3	17.0
TCA inlet liquor percent gypsum saturation	90	85	90	125	90	75	100
Percent sulfite oxidation	16	12	10	21	14	10	9
Percent lime utilization	91	93	92	92	92	88	90
TCA inlet pH	7.0	7.0	6.95	7.0	7.2	6.95	6.95
Adipic acid concentration, ppm	0	0	420	0	615	1305	1235
Centrifuge cake solids, wt %	63	63	61	60	55	57	60
Mist eliminator restriction, percent	0.2	1	1	-	-	-	0

Note: (1) All runs were made with 3 beds and 5 inches per bed of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres.

(2) DC=scrubber downcomer, EHT=effluent hold tank.

normally sufficient in the respective systems for the reagent dissolution and the gypsum desupersaturation. Lime systems usually give lower natural oxidation than limestone systems. Furthermore, the solubility of lime is about 100 times that of limestone and, hence, the lime dissolution rate is not a controlling factor.

14.1.1 Effect of Adipic Acid Concentration

By comparing Runs 976-2B and 977-2A with lime addition to the downcomer, it is seen that SO_2 removal increased from 67 percent without adipic acid to 80 percent with only 420 ppm adipic acid.

For Runs 978-2A, 979-2A, and 980-2A with lime addition to the effluent hold tank, SO_2 removals were 83, 93, and 97.5 percent with 0, 615, and 1305 ppm of adipic acid, respectively. Thus, with 600 to 1300 ppm adipic acid, SO_2 removal improved by 10 to 15 percentage points over the base case without the acid.

14.1.2 Effect of Slurry Flow Rate

Run 981-2A was made with a reduced slurry flow rate of 900 gpm, compared to 1200 gpm for Run 980-2A. Other operating conditions were the same for the two runs. As a result of the reduced slurry flow rate, the liquid-to-gas ratio decreased from 50 to 37 gal/mcf and the effluent hold tank residence time increased from 4.1 to 5.4 minutes. As expected, SO_2 removal dropped from 97.5 percent at 2750 ppm inlet SO_2 concentration to 92 percent at 2600 ppm inlet SO_2 concentration. SO_2 make-per-pass increased from 14.3 to 17.0 m-moles/liter. Average adipic acid concentration was slightly lower at 1235 ppm for Run 981-2A.

14.2 SUMMARY

At a scrubber inlet pH of 7 and a liquid-to-gas ratio of 50 gal/mcf, adipic acid-enhanced lime scrubbing improved the SO_2 removal by 10 to 15 percentage points with 600 to 1300 ppm adipic acid over the base case SO_2 removal of 83 percent without adipic acid. Reducing the liquid-to-gas ratio to 37 gal/mcf at 1235 ppm adipic acid and 7.0 scrubber inlet pH still yielded a good SO_2 removal of 92 percent.

Section 15

TCA LONG-TERM RELIABILITY LIME TEST WITH ONE-SCRUBBER-LOOP AND WITHOUT FORCED OXIDATION

A long-term reliability lime test, Run 625-2A, was conducted from November 10, 1978 through January 25, 1979, on the TCA system using one tank without forced oxidation. Adipic acid was not used in the run.

As with the venturi/spray tower limestone/adipic acid long-term reliability Run 907-1B (Section 4.2.6), Run 625-2A was made so that the EPA could assess continuous flue gas monitoring procedures. Another objective of the run was to continue the demonstration of the long-term operating reliability of the TCA lime system.

The major test conditions and average test results are listed in Table 15-1. The flue gas flow rate was varied between 17,000 and 30,000 acfm (gas velocity between 7.1 and 12.5 ft/sec) based on a "typical" daily boiler load cycle similar to that for Run 907-1B. The slurry flow rate was constant at 1450 gpm (L/G = 60 to 106 gal/mcf). The scrubber inlet pH was controlled at 8. Three beds were used, with 5 inches static height of 1-7/8 inch-diameter, 11.5-gram nitrile foam spheres in each bed.

Run 625-2A operated onstream for a total of 1652 hours. The scrubber onstream factor was 99.8 percent based on a total of 4 hours of unscheduled outages, excluding a 139-hour boiler outage and scheduled outages for routine inspection.

Table 15-1

RESULTS OF TCA LIME LONG-TERM RELIABILITY RUN 625-2A

Major Test Conditions	Run 625-2A
Fly ash loading	High
Gas rate, acfm @ 300°F	17,000-30,000(1)
Slurry flow rate, gpm	1450
Slurry solids concentration, wt %	8
TCA inlet pH controlled at	8.0
EHT residence time, min.	3.4
EHT level, ft	17
Lime addition point	DC/EHT(2)
Total static bed height, inches(3)	15
Run-Average Results	
Start-of-Run date	11/10/78
Onstream hours	1652
Percent SO_2 removal	90
Inlet SO_2 concentration, ppm	2350
SO_2 make-per-pass, m-moles/l	4-12
TCA inlet liquor percent gypsum saturation	105
Percent sulfite oxidation	16
Percent lime utilization	87

Notes:

(1) Gas rate was varied in accordance with a "typical" daily boiler load cycle.

(2) On 11/27/78 lime addition point was moved from the scrubber downcomer (DC) to EHT.

(3) Three beds, with 5 inches/bed of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres.

The average SO_2 removal for the run was 90 percent at 2350 ppm average inlet SO_2 concentration. Lime utilization averaged 87 percent at the controlled scrubber inlet pH of 8.0. The centrifuge was used in series with the clarifier. Average centrifuge cake solids content was 58 percent. Inspections after 388 hours and 1652 hours (end of run) showed that the mist eliminator was entirely clean and the scrubber was free of plugging and scaling. There was no increase in solids deposits on the scrubber internals during Run 625-2A.

Section 16

TCA LIME/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND ONE-TANK FORCED OXIDATION

Within-scrubber-loop forced oxidation in a single-loop scrubbing system would not be expected to give good SO_2 removal for a lime scrubber because of the oxidation of the major scrubbing species, sulfite ion, into non-reactive sulfate ion. With adipic acid addition, however, satisfactory SO_2 removal should be possible in a lime scrubber employing within-loop forced oxidation, because calcium adipate becomes the major scrubbing species. In addition, the lower pH at which a lime/adipic acid system operates should facilitate sulfite oxidation. All runs in this test series utilized 1200 ppm adipic acid.

16.1 SYSTEM DESCRIPTION

The flow diagram for the adipic acid-enhaced scrubbing in the single-loop TCA system with one tank and forced oxidation is shown in Figure 16-1. Adipic acid was added as a dry powder to the effluent hold tank (oxidation tank). Air was sparged into the tank through a simple 3-inch pipe ell. The arrangement of the oxidation tank is shown in Figure 16-2 which is drawn roughly to scale. The oxidation tank is 7 ft in diameter and was operated at 17-ft level in all runs in this test series. The agitator in the oxidation tank has two downflow turbines. Each turbine is 55 inches in diameter and contains 4 blades. Each blade on the bottom turbine has a stabilizing fin. The bottom turbine is about 20

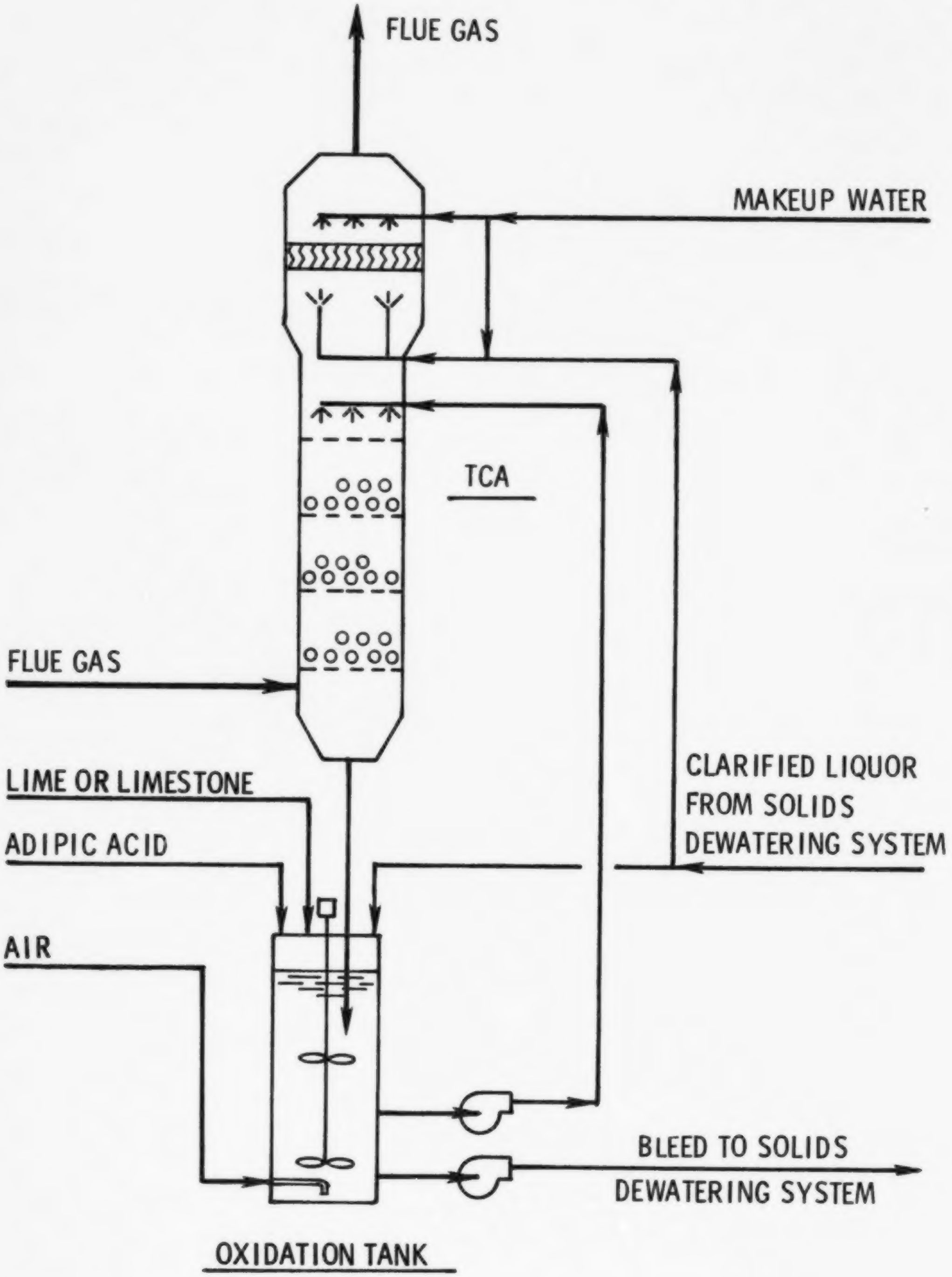

FLUE GAS
MAKEUP WATER
TCA
FLUE GAS
LIME OR LIMESTONE
ADIPIC ACID
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
AIR
BLEED TO SOLIDS DEWATERING SYSTEM
OXIDATION TANK

Figure 16-1. Flow Diagram For Adipic Acid-Enhanced Lime Or Limestone Scrubbing In The TCA System With One Tank And Forced Oxidation

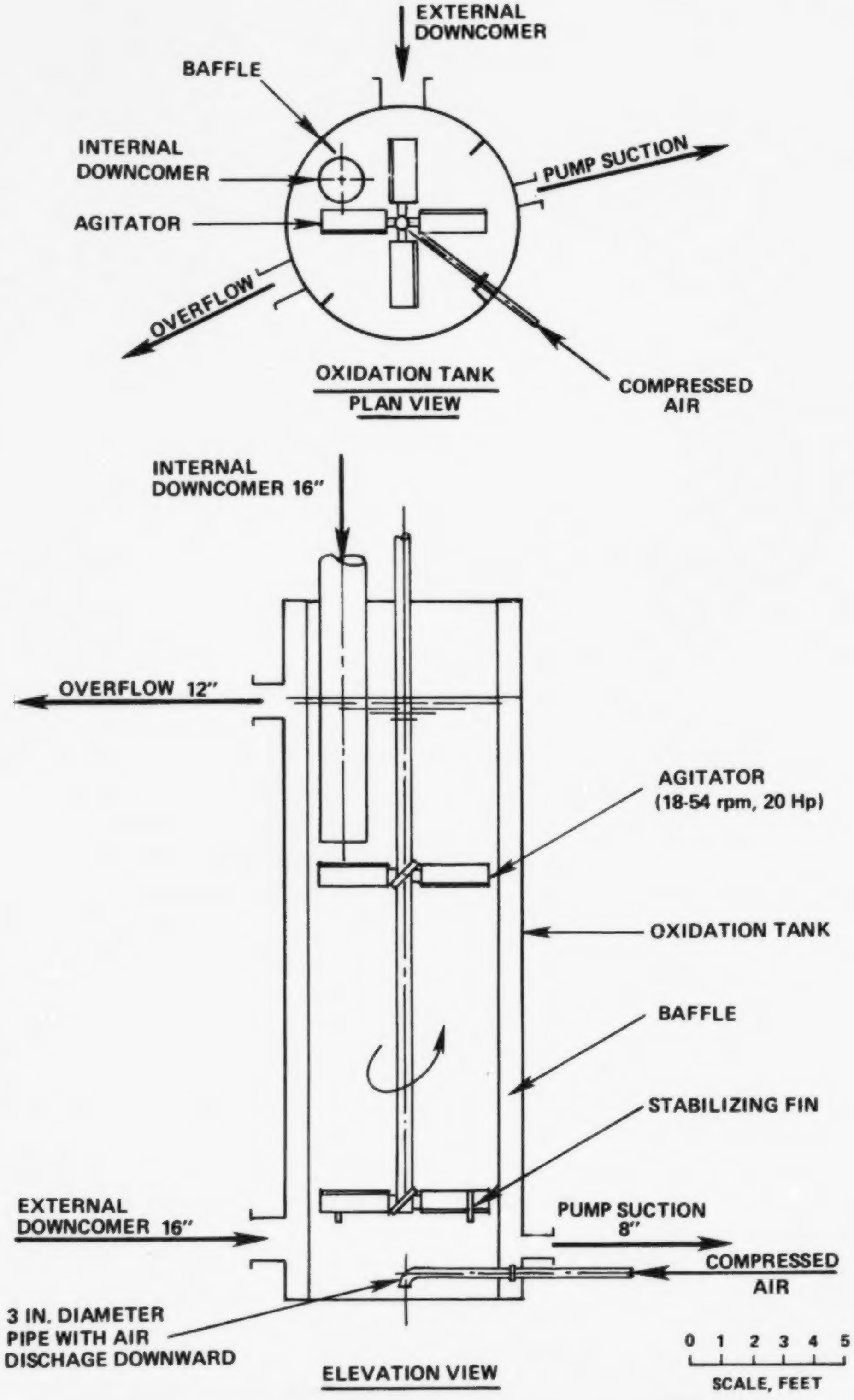

EXTERNAL DOWNCOMER
BAFFLE
INTERNAL DOWNCOMER
AGITATOR
PUMP SUCTION
OVERFLOW
COMPRESSED AIR
OXIDATION TANK
PLAN VIEW
INTERNAL DOWNCOMER 16"
OVERFLOW 12"
AGITATOR (18-54 rpm, 20 Hp)
OXIDATION TANK
BAFFLE
STABILIZING FIN
EXTERNAL DOWNCOMER 16"
PUMP SUCTION 8"
COMPRESSED AIR
3 IN. DIAMETER PIPE WITH AIR DISCHAGE DOWNWARD
ELEVATION VIEW
0 1 2 3 4 5
SCALE, FEET

Figure 16-2. ARRANGEMENT OF THE TCA OXIDATION TANK (D-204)

inches above the air sparger. The agitator has a 20 Hp motor and the speed can be varied between 18 and 54 rpm. The speed was set at 54 rpm for the test. The internal scrubber downcomer was used. The clarifier and centrifuge in series were used for solids dewatering.

16.2 DISCUSSION OF TEST RESULTS

Five runs were made from mid-March through early April 1979. Table 16-1 shows a summary of major test conditions and average results for these runs. Operating conditions for all runs were the same except that the TCA inlet pH was varied from run to run in order to seek an optimum pH range for good SO_2 removal as well as good sulfite oxidation.

Run 951-2A. The first test was made at a TCA inlet pH of 7.0. The test conditions for this run were the same as Run 980-2A (Table 14-1) except that 185 scfm of air was introduced to the oxidizer during Run 951-2A. Sulfite oxidation increased from 10 percent for Run 980-2A without air to only 47 percent for Run 951-2A with an air stoichiometry of 1.4 atoms oxygen/mole SO_2 absorbed. This resulted in a slight increase in centrifuge cake solids from 57 percent to 61 percent. The SO_2 removal remained high at 97 percent at 2800 ppm inlet SO_2 concentration.

Run 951-2B. To improve sulfite oxidation, the TCA inlet pH was lowered to 5.5. Oxidation increased to 88 percent while the SO_2 removal remained high at 95 percent with 2550 ppm inlet SO_2 concentration. The centrifuge cake solids content increased further to 74 percent. The high SO_2 removal obtained in this run was later attributed partly to high scrubber pressure drop caused by calcium sulfite scaling, as will be explained later.

Table 16-1

RESULTS OF ONE-SCRUBBER-LOOP TCA LIME/ADIPIC ACID TESTS WITH ONE-TANK FORCED OXIDATION

Major Test Conditions(1)	951-2A	951-2B	951-2C	951-2D	951-2E
Fly ash loading	High	High	High	High	High
Adipic acid concentration, ppm	1200	1200	1200	1200	1200
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000
Liquor rate, gpm	1200	1200	1200	1200	1200
Percent solids recirculated	8	8	8	8	8
TCA inlet pH (controlled)	7.0	5.5	5.0	4.5	5.0
Oxidation tank residence time (min)/Tank level (ft)	4.1/17	4.1/17	4.1/17	4.1/17	4.1/17
Lime addition point	Oxid. Tk	Oxid. Tk	Oxid. Tk	Oxid. Tk	Oxid. Tk
Air rate to oxidizer, scfm(2)	185	185	185	185	185
Run-Average Results					
Start-of-Run date	3/15/79	3/20/79	3/24/79	3/28/79	3/31/79
Onstream hours	57	102	89	64	103
Percent SO_2 removal	97	95	93	85	82
Inlet SO_2 concentration, ppm	2800	2550	2550	2150	2400
SO_2 make-per-pass, m-moles/l	14.4	12.8	12.5	9.7	10.4
TCA inlet liquor $SO_3^=$ concentration, ppm	165	245	230	80	100
TCA inlet liquor percent gypsum saturation	105	115	110	110	105
Slurry percent solids	8.8	8.0	8.2	7.8	7.8
Percent sulfite oxidation	47	88	95	96	98
Percent lime utilization	93	96	97	98	97
TCA inlet pH	7.0	5.5	5.0	4.6	4.95
Adipic acid concentration	1215	1230	1270	1260	1330
Centrifuge cake solids, wt%	61	74	74	71	72
Air stoichiometry, atoms O/mole SO_2 absorbed	1.40	1.55	1.60	2.05	1.95
Mist eliminator restriction, %	-	-	-	0	-

Notes: (1) All runs were made with 3 beds and 5 inches/bed of 1-7/8 inch diameter nitrile foam spheres. Internal D-204 downcomer was used in all runs.

(2) A single 3-inch diameter pipe was used. Air discharged downward at center of oxidation tank 5 inches from tank bottom.

Run 951-2C. The scrubber inlet pH was further reduced to 5.0 in this run. Oxidation continued to increase to 95 percent, while SO_2 removal again remained high at 93 percent at 2550 ppm inlet SO_2 concentration. As in Run 951-2B, the unexpectedly high SO_2 removal was attributed partly to high scrubber pressure drop. At an inlet pH of 5.0 it is expected that calcium adipate is the main SO_2 scrubbing medium with very little scrubbing contributed by other species such as hydrated lime or unoxidized sulfite in a forced oxidation system.

Run 951-2D. Because of the apparently high SO_2 removal at an inlet pH of 5.0, the pH was further reduced to 4.5. At this low pH adipic acid should not be fully effective and a drop in SO_2 removal should result. The SO_2 removal indeed dropped to 85 percent at a decreased inlet SO_2 concentration of 2150 ppm. The combination of low pH and high air stoichiometry of 2.05 atoms oxygen/mole SO_2 absorbed resulted in a good oxidation of 96 percent. The high air stoichiometry was the result of a drop in both SO_2 removal and inlet SO_2 concentration.

Run 951-2E. The purpose of Run 951-2E was to confirm the excellent SO_2 removal obtained at the low inlet pH of 5.0 during Run 951-2C. However, differences in system pressure drop (total pressure drop across the TCA minus mist eliminator pressure drop) between the two runs precluded exact replication.

In Run 951-2C, the system pressure drop was erratic and averaged about 11 inches H_2O. In Run 951-2E, the average system pressure drop was only 8.5 inches H_2O with the last two-thirds of the run operating below 8.0 inches H_2O. Somewhat higher than normal system pressure drop of 9 inches H_2O was also observed during Run 951-2B. Normal system pressure drop, under the operating conditions listed in Table 16-1, is usually 7 to 8 inches H_2O when the system is clean. The cause of the pressure drop variation was attributed to scaling and descaling of calcium sulfite.

At the lower system pressure drop during Run 951-2E, as compared to Run 951-2C, SO_2 removal dropped to 82 percent at 2400 ppm inlet SO_2 concentration.

It should be noted that an SO_2 removal of about 65 percent would be predicted under the same operating conditions as Run 951-2E but without forced oxidation and without adipic acid addition. Without adipic acid and with forced oxidation, SO_2 removal should be significantly lower than 65 percent.

Calcium Sulfite Scaling. As mentioned previously, the system pressure drop varied throughout this test series, which was most likely caused by scaling and descaling of calcium sulfite. Scaling appeared to begin during Run 951-2A at a high inlet pH of 7.0 and a high SO_2 make-per-pass of 14.4 m-moles/liter, and continued during Run 951-2B when the pH was reduced to 5.5 but at a rather high SO_2 make-per-pass of 12.8 m-moles/liter. Sulfite descaling began during Run 951-2C at an inlet pH of 5.0, and continued through Runs 951-2D (4.5 inlet pH) and 951-2E (5.0 inlet pH) at an SO_2 make-per-pass of about 10 m-moles/liter.

Several factors may have contributed to the sulfite scaling. Adipic acid buffered the pH drop across the scrubber and the higher outlet pH, especially at a high inlet pH of 7.0, caused sulfite supersaturation in the scrubber outlet liquor. High SO_2 make-per-pass, from the high SO_2 removal due to adipic acid addition, undoubtedly contributed to the sulfite supersaturation in the scrubber outlet liquor. Forced oxidation depleted the $CaSO_3$ solids which would otherwise be available for sulfite desupersaturation.

16.3 SUMMARY

The following is a summary of the test results:

- Within-scrubber-loop forced oxidation of sulfite to sulfate is feasible in a single-loop adipic acid-enhanced lime system. Under this condition calcium adipate becomes the major scrubbing species.

- Optimum scrubber inlet pH appeared to be about 5.0, with respect to SO_2 removal, sulfite oxidation, and calcium sulfite scaling.
- At 5.0 scrubber inlet pH and 1330 ppm adipic acid concentration (Run 951-2E), good SO_2 removal of 82 percent and near complete oxidation of 98 percent were achieved under the operating conditions typical for the TCA. SO_2 removal greater than 82 percent should be easily achieved by raising the adipic acid concentration above the 1330 ppm tested.
- Calcium sulfite supersaturation and the resultant scaling could occur under combinations of high pH (5.5 or higher at the scrubber inlet), forced oxidation (low $CaSO_3$ solids concentration), and high SO_2 make-per-pass.

Section 17

TCA LIMESTONE/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND ONE-TANK FORCED-OXIDATION

This series of tests was originally intended to be a study of the effects of various agitator speeds and air rates on the degree of sulfite oxidation. During the initial run, however, the system behaved as though the limestone was being blinded. The limestone feed rate rose sharply as the attempt was made to maintain the TCA inlet pH above 5.1. Limestone utilization ranged as low as 25 percent and averaged 38 percent. Concurrent with the drop in limestone utilization was a substantial increase in the apparent sulfite ion concentration (by amperometric titration for total oxidizable sulfite) in the liquor entering the scrubber. The average inlet $SO_3^=$ concentration rose to 1510 ppm. Such concentrations are an order of magnitude above the normal sulfite values which normally average below 200 ppm in a forced oxidation system.

Under such abnormal conditions, the plans for an agitator/air rate study were postponed and replaced by a series of tests designed to give additional information as to the cause of the abnormal system behavior.

The flow configuration for the adipic acid-enhanced limestone tests using one tank and forced oxidation is the same as that shown in Figure 16-1. Details of the oxidation tank arrangement are shown in Figure 16-2.

17.1 DISCUSSION OF TEST RESULTS

Table 17-1 lists the major test conditions and run-average results for six runs conducted in April 1979. Major independent variables investigated were air flow rate (air stoichiometry) and limestone and adipic acid addition points, to observe their effects on system instability with respect to high liquor sulfite concentration and low limestone utilization (low pH). The effect of oxidation tank residence time was also investigated briefly. All runs were made with 1500 ppm adipic acid, 15 percent slurry solids concentration, and flue gas with high fly ash loading.

17.1.1 Effect of Air Stoichiometry

In the initial phase of Run 901-2A (see Part 1 for this run in Table 17-1) during which the abnormal conditions described above occurred (38 percent limestone utilization and 1510 ppm inlet liquor sulfite concentration), both the fresh limestone and adipic acid were fed to the oxidation tank as shown in Figure 16-1. Air was fed to the oxidation tank at a rate of 185 scfm which gave an air stoichiometric ratio of 1.6 atoms oxygen/mole SO_2 absorbed. Average adipic acid concentration was 1530 ppm.

In the second phase of Run 901-2A the air was turned off to find out if the unusual system behavior would continue or if the system would return to normal. The TCA had been operated successfully many times before without forced oxidation using the same configuration (see Section 13). Within hours after the air had been stopped, the sulfite concentration dropped to a near normal level of 320 ppm and limestone utilization increased to 84 percent. The SO_2 removal remained high at better than 95 percent with an inlet SO_2 concentration of 2635

Table 17-1

RESULTS OF ONE-SCRUBBER-LOOP TCA LIMESTONE/ADIPIC ACID TESTS WITH ONE-TANK FORCED OXIDATION

Major Test Conditions	901-2A					901-2H	901-2I	901-2J		902-2A	902-2B
	1	2	3	4	5			1	2		
Fly ash loading	High					High	High	High	High	High	High
Adipic acid concentration, ppm	1500					1500	1500(2)	1500	1500	1500	1500
Gas rate, acfm @ 300°F	30,000					30,000	30,000	30,000	30,000	22,500	22,500
Liquor rate, gpm	1200					1200	1200	1200	1200	900	900
Percent solids recirculated	15					15	15	15	15	15	15
TCA inlet pH (controlled)	- (1)	- (1)	5.2	- (1)	5.2	5.2	5.4(3)	-	5.2	-	-
Limestone stoich. ratio (controlled)	1.2	1.2		1.2	-	-	-	1.2	-	1.2	1.2
Residence time, min.	4.1					4.1	4.1	4.1	4.1	5.5	5.5
Tank level, ft.	17					17	17	17	17	17	17
Limestone addition point(4)	D-204					G-201	G-201	D-204	D-204	D-204	D-204
Air rate to oxidizer, scfm	185	0	185	300	185	185	185	0	160(5)	110(5)	135(6)
Run-Average Results											
Start-of-run date	4/6/79	4/10/79	4/11/79	4/12/79	4/14/79	4/15/79	4/19/79	4/25/79	4/27/79	4/28/79	4/30/79
Onstream hours	91	23	28	45	21	94	92	63	33	51	39
Percent SO_2 removal	93.6	95.5	95.4	97.3	97.1	97.3	96.9	92.7	93.0	91.8	88.5
Inlet SO_2 concentration, ppm	2545	2635	2400	2530	2400	2275	2300	2460	2490	2255	2575
SO_2 make-per-pass, m-moles/l	12.6	13.1	12.1	13.2	12.6	11.5	11.8	12.0	11.9	11.2	11.8
Inlet liquor $SO_3^=$ concentration, ppm	1510	320	810	85	825	220	330	325	1055	675	1145
TCA inlet liquor percent gypsum sat'n	135	125	130	110	130	110	120	120	120	130	135
Slurry percent solids	14.6	13.7	14.6	13.6	15.2	15.2	15.0	13.9	14.9	14.8	14.7
Percent sulfite oxidation	97.5	17.5	96.0	99.3	97.5	99.0	98.5	24.0	94.0	98.6	97.5
Percent limestone utilization	38	84	55	88	41	65	47	86	45	50	56
Inlet pH	5.0	5.3	5.2	5.3	5.4	5.3	5.3	5.4	5.1	5.2	5.1
Adipic acid concentration, ppm	1530	1482	1395	1495	1390	1575	1530	1525	1485	1550	1450
Centrifuge cake solids, wt %	77	60	78	73	78	77	78	63	75	78	77
Air stoichiometry, atoms O/mole SO_2 abs.	1.60	0	1.70	2.45	1.65	1.75	1.70	0	1.45	1.45	1.60
Mist eliminator restriction, %	-	-	-	-	-	-	0	-	-	-	0

Notes:
(1) pH underride 5.2 changed to 4.9 early in run.
(2) Adipic acid added to clarifier overflow receiving tank.
(3) Changed during run to 5.2.
(4) D-204 is the oxidation tank while G-201 refers to the suction of the slurry recirculation pump.
(5) Air controlled to maintain a 1.45 air stoichiometry with a 1.55 max.
(6) Air controlled to maintain a 1.60 air stoichiometry.

ppm. The sulfite oxidation in the solids dropped to 18 percent, normal for a run without forced oxidation.

The air was again introduced to the oxidizer at a rate of 185 scfm during the third phase of Run 901-2A. The purpose was to see if the unusual behave experienced in Part 1 of the run was a transient phenomenon or could be repeated. The answer came within a few hours as the inlet pH level fell and the limestone addition rate had to be increased to maintain the inlet pH at 5.2. Liquor sulfite level also began to climb. When the system finally leveled out, the limestone utilization dropped to 55 percent and the liquor sulfite level averaged 810 ppm. As with the first two phases, the SO_2 removal remained unaffected at greater than 95 percent with 2400 ppm SO_2 in the flue gas. The oxidation had returned to near its earlier value of 96 percent.

In the fourth phase of Run 901-2A, the air was increased to 300 scfm to see what effect the increased oxygen would have on the high liquor sulfite level. The resulting air stoichiometric ratio was 2.45 atoms oxygen/mole SO_2 absorbed. It was hypothesized that adipic acid or its degraded products might have formed complexes with sulfite in the liquor which were more difficult to oxidize. The hypothesis, however, could not be substantiated by the ion chromatograph and infrared analysis of the liquor species. Part 2 of Run 901-2J was made to provide the high sulfite samples for these analyses (Part 1 of Run 901-2J was made without air due to an air compressor failure).

Once again the results were quick to come. Within a few hours of the air rate increase in Part 4 of Run 901-2A, the sulfite level dropped to only 85 ppm and limestone utilization rose to 88 percent. In addition, SO_2 removal increased to better than 97 percent despite a slight rise in inlet SO_2 concentration to 2530 ppm. As would be expected the oxidation reached a high of 99.3 percent.

To further document the unusual conditions experienced in phases 1 and 3 of Run 901-2A, and to provide additional samples of the liquor, the air rate was once more returned to the original rate of 185 scfm during the fifth phase of Run 901-2A. Again the system responded with an increased liquor sulfite level of 825 ppm and more limestone was again required to maintain pH control. Limestone utilization dropped to 41 percent. SO_2 removal and oxidation remained high, both at 97 percent.

17.1.2 Effect of Limestone Addition Point

Based on the results of Run 901-2A it was apparent that the high sulfite/low limestone utilization phenomenon was real and reproducible. A close examination of the IERL-RTP pilot plant test results (Reference 10) with limestone/adipic acid and with single-loop forced oxidation indicated that the high sulfite/low limestone utilization phenomenon observed at Shawnee did not exist in the pilot plant where limestone was added to a separate hold tank downstream of the oxidation tank.

In Run 901-2H* the limestone addition point was moved to the suction of the recirculated slurry pump. This removed fresh limestone from the oxidation tank but did not provide the additional residence time found in the IERL-RTP pilot plant tests utilizing a second hold tank. The resulting configuration was somewhere between that used in 901-2A and that used at the IERL-RTP pilot plant. The results reflected the compromise. While the average liquor sulfite level was reduced to 220 ppm, the limestone utilization improved but remained low at

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*Runs 901-2B through 901-2G were originally part of the scheduled agitator/air rate study and were not made because of the change of the test objective in this test series.

65 percent. The modification did not affect the SO_2 removal or the oxidation which were 97 percent and 99 percent, respectively.

17.1.3 Effect of Adipic Acid Addition Point

A second difference between the IERL-RTP equipment configuration (Reference 10) and that used in this test series was that the addition of adipic acid was also outside the oxidation tank. At the IERL-RTP pilot plant the acid was added in a small receiving tank between the scrubber and the oxidation tank. Since one theory which had been proposed was that the sulfite might be complexing with the adipic acid or its degraded products, relocation of the adipic acid feed might have an effect on the test results. In Run 901-2I the adipic acid was added to the process water hold tank (clarified liquor receiving tank) which received the clarifier overflow and centrate. The results showed no apparent effect over that experienced in Run 901-2H. The sulfite level increased slightly to 330 ppm while limestone utilization dropped to 47 percent. The SO_2 removal was 97 percent and oxidation was 98.5 percent.

17.1.4 Effect of Oxidation Tank Residence Time

In Part 4 of Run 901-2A, it had been demonstrated that sufficient air could oxidize the liquor sulfite that was being accumulated. In Runs 902-2A and 902-2B, both the flue gas and slurry flow rates were reduced to 22,500 acfm and 900 gpm, respectively, to increase the oxidation tank residence time (with respect to both slurry bleed rate and recirculation rate) in the hope that this would facilitate the oxidation of liquor sulfite. Unfortunately, the magnitude of change was small and the higher residence time of 5.5 minutes (with respect to 900 gpm recirculated slurry rate) was apparently insufficient to cause a significant change in the test results. The SO_2 removal dropped to about 90 percent for the two runs at the reduced slurry flow rate of 900 gpm.

17.1.5 Limestone Blinding and $CaSO_3$ Supersaturation

The phenomenon of high liquor sulfite/low limestone utilization can best be explained by referring to the discussions presented in Sections 6 and 16 on the same subject. High levels of solids oxidation, as in the within-loop-oxidation of a single-loop system, or second loop of a two-loop system with recycle of oxidized slurry from the first loop (oxidation loop), leave insufficient $CaSO_3$ solid crystals for sulfite desupersaturation. If a particular system configuration, as in the second loop of a two-loop system, requires $CaSO_3$ precipitation in the scrubber, excessive $CaSO_3$ supersaturation would result. Even if $CaSO_3$ precipitation is not required, as in the present series with a single loop and forced oxidation, high levels of dissolved sulfite, and therefore supersaturation, can result from insufficient oxidation intensity.

Excessive $CaSO_3$ supersaturation results in $CaSO_3$ scaling (in case of a lime system) or limestone blinding. The latter subsequently causes low pH and poor limestone utilization.

In a single-loop system with forced oxidation, however, the effect of $CaSO_3$ supersaturation can be avoided by operating the oxidizer with excess air (as in Part 4 of Run 901-2A). Single-loop operation without forced oxidation should give sufficient $CaSO_3$ solids for sulfite desupersaturation (as in Part 2 of Run 901-2A when no air was used).

Adipic acid addition increases the $CaSO_3$ supersaturation potential because of the higher SO_2 make-per-pass it produces and the decreased pH drop across the scrubber (due to the buffering effect of adipic acid). With proper selection of test conditions, however, this would not be a problem.

Limestone blinding is discussed in more detail in Section 25.

17.2 SUMMARY

The following is a summary of the results of testing on the TCA with limestone/adipic acid with forced oxidation using one tank:

- Calcium sulfite supersaturation and blinding of limestone, resulting in low pH and/or poor limestone utilization, could result from insufficient oxidation intensity in a single-loop forced oxidation system. Air stoichiometry necessary to avoid this situation appeared to be greater than about 1.7 atoms oxygen/mole SO_2 absorbed under the conditions tested (1500 ppm adipic acid).
- Despite the high liquor sulfite/low limestone utilization phenomenon, SO_2 removal greater than 92 percent was achieved at 1500 ppm adipic acid concentration and 5.0-5.4 scrubber inlet pH under typical TCA operating conditions. Sulfite oxidation greater than 95 percent was obtained with air stoichiometries as low as 1.45 atoms oxygen/mole SO_2 absorbed.

Section 18

TCA LIMESTONE/ADIPIC ACID TESTS WITH ONE-SCRUBBER-LOOP AND TWO-TANK FORCED-OXIDATION

Adipic acid-enhanced limestone test results from the TCA system with forced oxidation using a single tank (see Section 17) indicated that high liquor sulfite and limestone blinding could result from insufficient oxidation intensity. In those tests, limitation in the size of the oxidation tank prevented testing of the effect of higher oxidation tank residence times (up to 5.5 minutes in Runs 902-2A and 902-2B, Table 17-1).

As mentioned in Section 17, limestone/adipic acid tests at the IERL-RTP pilot plant (Reference 10) with forced oxidation using two tanks (oxidation tank followed by a second hold tank where limestone was added) did not produce the high liquor sulfite/low limestone utilization phenomen observed at Shawnee. Operation with two tanks in series with limestone added to the second tank has several advantages over the single-tank operation. These advantages have been previously listed in Section 10.

18.1 SYSTEM DESCRIPTION

Figure 18-1 shows a flow diagram for the adipic acid-enhanced limestone scrubbing in the single-loop TCA system with forced oxidation using two tanks. Adipic acid was added as a dry powder to the oxidation tank (the first tank) while limestone was added to the effluent hold tank (the second tank). The detailed

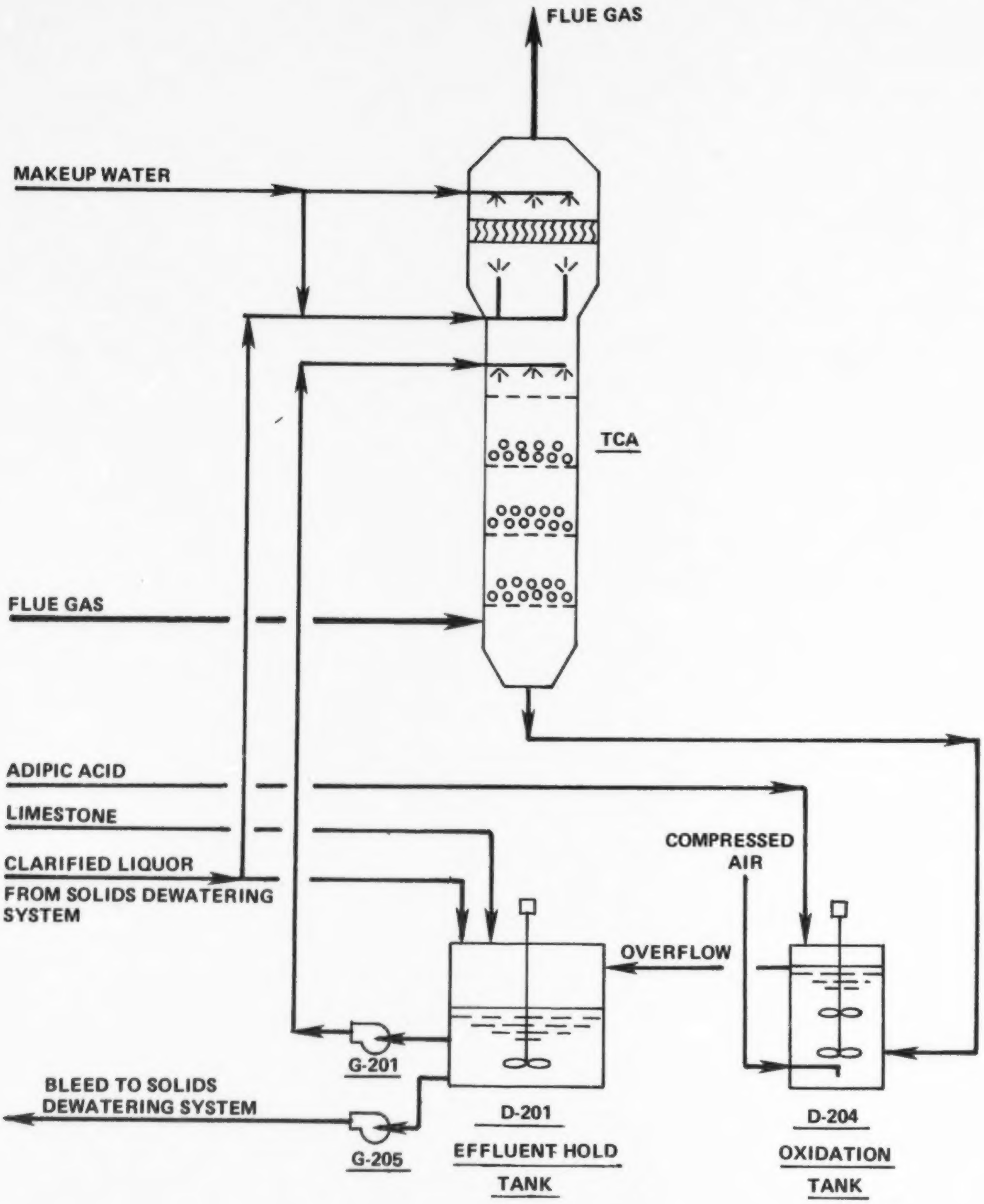
FLUE GAS
MAKEUP WATER
TCA
FLUE GAS
ADIPIC ACID
LIMESTONE
CLARIFIED LIQUOR
FROM SOLIDS DEWATERING
SYSTEM
COMPRESSED
AIR
OVERFLOW
G-201
BLEED TO SOLIDS
DEWATERING SYSTEM
G-205
D-201
EFFLUENT HOLD
TANK
D-204
OXIDATION
TANK

Figure 18-1. Flow Diagram For One-Scrubber-Loop Forced Oxidation In The TCA System Using Two Tanks

arrangement of the oxidation tank is shown in Figure 16-2. The external downcomer of the oxidation tank was used in this test series.

18.2 DISCUSSION OF TEST RESULTS

Two runs (Runs 903-2A and 903-2B) were made with 1500 ppm adipic acid in the first half of May 1979 before a series of limestone/adipic acid factorial tests (see Section 22). Four additional runs (Runs 906-2A through 906-2D) were conducted in mid-October 1979 to cover a wider range of adipic acid concentration, including an adipic acid depletion test from 2000 ppm to 800 ppm and one from 800 ppm to 400 ppm. Table 18-1 summarizes the major test conditions and run-average results.

18.2.1 Effect of Two-tank vs. One-tank Operation

Run 903-2A (Table 18-1) was made under the same operating conditions as Run 901-2A (Table 17-1) except for the number of tanks used. Relocation of the limestone feed to the second tank in Run 903-2A proved to be successful in solving the high liquor sulfite/low limestone utilization problem experienced in the single-tank mode. A comparison of the results from Part 1 of Run 901-2A and Run 903-2A clearly shows the advantages of two-tank operation:

	Run 901-2A Part 1	Run 903-2A
Number of tanks	1	2
Percent SO_2 removal	93.6	93.8
Inlet SO_2 conc., ppm	2545	2680
SO_2 make-per-pass, m-moles/l	12.6	13.2
Inlet liquor $SO_3^{=}$ conc., ppm	1510	55
Inlet liquor percent gypsum sat'n	135	95
Percent sulfite oxidation	97.5	99.1
Percent limestone utilization	38	90
Inlet pH	5.0	5.3
Adipic acid conc., ppm	1530	1550
Air stoich., atoms O/mole SO_2 abs.	1.6	1.5

Table 18-1

RESULTS OF ONE-SCRUBBER-LOOP TCA LIMESTONE/ADIPIC ACID TESTS WITH FORCED OXIDATION USING TWO TANKS

Major Test Conditions	903-2A	903-2B	906-2A(3)	906-2B	906-2C	906-2D(3)
Fly ash loading	High	High	High	High	High	High
Adipic acid concentration, ppm	1500	1500	2000 → 800	800	800	800 → 400
Gas rate, acfm @ 300°F	30,000	30,000(1)	25,000	25,000	25,000	25,000
Liquor rate, gpm	1200	1200	1200	1200	1200	1200
Percent solids recirculated	15	15	15	15	15	15
Limestone stoich. ratio (controlled)	1.2	1.2	1.2	1.2	1.2	1.2
Res. time (min)/Tk level (ft):						
Oxidation Tank (D-204)	4.3/18	4.3/18	4.3/18	4.3/18	4.3/18	4.3/18
EHT (D-201)	12/6.1	12/6.1	12/6.1	12/6.1	12/6.1	12/6.1
Air rate to oxidizer, scfm	185	185	185	185	185	185
Run-Average Results						
Start-of-Run Date	5/2/79	5/9/79	10/11/79	10/17/79	10/18/79	10/19/79
Onstream hours	51	88	158	24	24	48
Percent SO_2 removal	93.8	96.2	98.1 → 94.8	95.3	96.5	96.9 → 93.6
Inlet SO_2 concentration, ppm	2680	2370	1940	2310	2220	2050
SO_2 make-per-pass, m-moles/l	13.2	12.1	8.3	9.7	9.5	8.6
Inlet liquor $SO_3^{=}$ concentration, ppm	55	70	40	95	25	30
Inlet liquor percent gypsum saturation	95	100	95	90	95	90
Slurry percent solids	14.4	15.2	15.0	15.1	14.8	14.8
Percent sulfite oxidation	99.1	99.5	99.2	99.3	99.5	99.6
Percent limestone utilization	90	86	82	88	78	81
Inlet pH	5.30	5.42	5.72	5.86	6.10	5.73
Adipic acid concentration, ppm	1550	1530	2115 → 830	770	850	860 → 600
Filter cake solids, wt %	78(2)	88(4)	86	(5)	88	87
Air stoich., atoms O/mole SO_2 absorbed	1.50	1.65	2.40	2.05	2.10	2.30
Mist eliminator restriction, %	0	-	-	-	-	-

(1) Flue gas from Unit 9
(2) Centrifuge cake solids
(3) Adipic acid depletion tests
(4) Horizontal belt filter cake solids
(5) Open-loop operation

With slightly lower air stoichiometry of 1.50 atoms oxygen/mole SO_2 absorbed, two-tank operation gave only 55 ppm of sulfite in the TCA inlet liquor compared to 1510 ppm for the one-tank mode. Limestone utilization was 90 percent with a TCA inlet pH of 5.3 for the two-tank mode, compared to 38 percent utilization and 5.0 inlet pH for the one-tank scheme. Higher sulfite oxidation and lower gypsum saturation were also observed for Run 903-2A.

For all runs made with two tanks, average inlet liquor sulfite never exceeded 100 ppm and limestone utilizations were all above about 80 percent at the controlled stoichiometry of 1.2. Higher pH's and lower gypsum saturations in the TCA inlet liquor were also observed. Sulfite oxidations were all greater than 99 percent.

18.2.2 Effect of Flue Gas Source

Based on the success of Run 903-2A, the two-tank configuration was chosen for the limestone/adipic acid forced oxidation factorial series (see Section 22) to be operated on flue gas from Boiler No. 9 during the 9-week maintenance outage of Boiler No. 10 (May-July 1979). In order to check the effect of the gas from Boiler No. 9, Run 903-2B was made under the same operating conditions as Run 903-2A except for the change of flue gas. The results for the two runs were consistent and no significant differences were discernible.

18.2.3 Effect of Adipic Acid Concentration on SO_2 Removal

In Runs 906-2A through 906-2D, the adipic acid concentration was decreased from 2000 ppm to 400 ppm to observe the effect on SO_2 removal.

Adipic acid was depleted from 2000 ppm to 800 ppm during Run 906-2A by reducing the acid addition rate under a closed-liquor-loop condition. It was then maintained at 800 ppm under a closed-liquor-loop condition during Run 906-2C. During Run 906-2D, adipic acid concentration was to be further depleted from 800 ppm to 400 ppm, again under a closed-loop condition and at a reduced addition rate. Final concentration, however, was 600 ppm, instead of the planned 400 ppm, because the TCA system had to be transferred to TVA for the demonstration of the DOWA basic aluminum sulfate scrubbing process.

During this series of tests (Runs 906-2A, 906-2C, and 906-2D), actual adipic acid concentration decreased from 2115 to 600 ppm while the SO_2 removal dropped from 98.1 to 93.6 percent, demonstrating good SO_2 removal with adipic acid concentration as low as 600 ppm. Scrubber inlet pH ranged from 5.7 to 6.1. Average inlet SO_2 concentration, however, was low during this series, ranging from 1940 to 2220 ppm.

18.2.4 Effect of Open-Liquor-Loop Operation

Run 906-2B was conducted with open-liquor-loop operation. The scrubber bleed slurry (15 percent solids) was discharged directly from the system, bypassing the clarifier and the rotary drum vacuum filter with no clarified liquor or filtrate returned to the scrubber loop. This mode of operation requires a much higher adipic acid addition rate, and since no degraded acid is returned by the clarified liquor or filtrate, the adipic acid existing in the scrubber loop should be relatively fresh and not degraded. Therefore, the effect of the "freshness" of adipic acid on SO_2 removal can be compared between the "fresh" acid in the open-loop operation (Run 906-2B) and the "degraded" acid in the closed-loop operation (Run 906-2C).

Little or no effect on the SO_2 removal was observed. The SO_2 removal was 96.5 percent at 2220 ppm inlet SO_2 concentration for Run 906-2C with closed-loop operation, compared to 95.3 percent removal at 2310 ppm inlet SO_2 concentration for Run 906-2B with open-loop mode. This observation is consistant with that made during venturi spray tower limestone/adipic acid factorial tests (see Section 22).

18.3 SUMMARY

The following is a summary of the results of limestone/adipic acid tests with forced oxidation using two tanks:

- Two-tank operation is superior to one-tank operation. With the two-tank mode, the high liquor sulfite and limestone blinding problem experienced with one-tank operation was eliminated. Furthermore, higher sulfite oxidation, higher scrubber inlet pH (or higher limestone utilization), and lower gypsum saturation were achieved with the two-tank scheme.

- No differences in the test results were discernible when flue gas from Boiler No. 9 or Boiler No. 10 was used.

- Good SO_2 removal of 93.6 percent was achieved with adipic acid concentration as low as 600 ppm at 2050 ppm inlet SO_2 concentration, a liquid-to-gas ratio of 60 gal/mcf, and 81 percent limestone utilization (5.73 scrubber inlet pH).

- At 800 ppm concentration, "freshness" (fresh vs. degraded) of adipic acid did not show an effect on SO_2 removal.

Section 19

EFFECTS OF AGITATOR SPEED AND AIR STOICHIOMETRY ON SULFITE OXIDATION AND LIMESTONE UTILIZATION IN THE TCA SYSTEM

The purpose of this test series was to investigate the effects of the oxidation tank agitator speed and the air stoichiometry on the degree of sulfite oxidation. Limestone slurry without adipic acid was used in the tests. A single tank was used to give a more sensitive oxidation response. The flow configuration and the arrangement of the oxidation tank are shown in Figures 16-1 and 16-2, respectively.

Table 19-1 lists the results of 30 runs made in this test series (9 runs in late June through early August 1979 and 21 runs in September 1979). Operating conditions common to all runs were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Gas flow rate:	30,000 acfm @ 300°F
Slurry flow rate:	1200 gpm
Slurry solids concentration:	15 percent
Limestone stoichiometry:	1.2 moles Ca/mole SO_2 absorbed (TCA inlet pH greater than 5.1)
Oxidation tank level:	17 ft (7 ft diameter)
Total static bed height:	15 inches of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres

Three levels of agitator speeds, 18, 36, and 54 rpm, were studied. Initially the air flow rate was fixed during a run (Runs 904-2A through 904-2G) to give the desired air stoichiometric ratio. However, because of the variation in inlet SO_2 concentration and the decreasing trend of the SO_2 concentration during

Table 19-1

RESULTS OF TCA LIMESTONE TESTS WITH FORCED OXIDATION USING ONE TANK - EFFECT OF AIR STOICHIOMETRY AND AGITATOR SPEED

Major Test Conditions	904-2A	904-2B	904-2C	904-2D	904-2E	904-2F	904-2G	904-2H	904-2I
Fly ash loading	High	High	High	High	High	High	High	High	High
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Liquor rate, gpm	1200	1200	1200	1200	1200	1200	1200	1200	1200
Percent solids recirculated	15	15	15	15	15	15	15	15	15
Limestone stoich. ratio(1) (controlled)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Oxidation tank residence time, min.	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
Tank level, ft.	17	17	17	17	17	17	17	17	17
Air rate to oxidizer, scfm	185	110	185	110	185	300	300	40(2)	40(2)
Oxidizer agitator speed, rpm	54	54	36	36	18	18	36	36	54
Run-Average Results									
Start-of-Run Date	6/26/79	6/3079	7/6/79	7/15/79	7/19/79	7/23/79	7/30/79	8/2/79	8/7/79
Onstream hours	97	124	144	94	100	46	71	125	40
Percent SO_2 removal	81.1	80.6	77.2	66.1	81.8	82.0	81.4	81.9	82.8
Inlet SO_2 concentration, ppm	2355	2165	2220	2315	1870	1965	1225	1165	1160
SO_2 make-per-pass, m-moles/l	10.1	9.2	9.2	8.3	8.1	8.3	5.3	5.1	5.2
Inlet liquor $SO_3^=$ concentration, ppm	244	226	96	1041	22	21	25	237	23
Inlet liquor percent gypsum saturation	115	110	110	155	110	95	95	110	90
Slurry percent solids	14.9	15.1	14.5	15.2	14.3	14.7	15.5	15.3	14.6
Percent sulfite oxidation	98.0	99.1	99.4	97.4	99.1	99.3	99.4	99.1	99.0
Percent limestone utilization	84	80	84	44	82	85	86	79	82
Inlet pH	5.50	5.40	5.30	5.15	5.25	5.40	5.55	5.40	5.30
Filter cake solids, wt %	85	86	88	81	86	86	-	-	-
Air stoichiometry, atoms O/ mole SO_2 abs.	2.01	1.29	2.24	1.48	2.49	3.81	6.10	0.85	0.85
Mist eliminator restriction, %	-	-	-	-	-	-	-	-	0

(1) pH underride of 5.2

(2) Run with air stoichiometry controlled at 1.0

Table 19-1 (continued)

RESULTS OF TCA LIMESTONE TESTS WITH FORCED OXIDATION USING ONE TANK - EFFECT OF AIR STOICHIOMETRY AND AGITATOR SPEED

Major Test Conditions	904-2J	904-2K	904-2L	904-2M	904-2N	904-2O	904-2P	904-2Q	904-2R	904-2S	904-2T	904-2U
Fly ash loading	High	High	High	High	High	High	High	High	High	High	High	High
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Liquor rate, gpm	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200
Percent solids recirculated	15	15	15	15	15	15	15	15	15	15	15	15
Limestone stoich. ratio(1) (controlled)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Oxidation tank residence time, min.	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1(3)	4.1(3)	4.1(3)
Tank level, ft.	17	17	17	17	17	17	17	17	17	17	17	17
Air rate to oxidizer, scfm(2)	93	114	118	140	196	160	151	233	210	117	149	208
Oxidizer agitator speed, rpm	54	54	54	36	36	36	18	18	18	54	36	18
Run-Average Results												
Start-of-Run Date	9/4/79	9/6/79	9/7/79	9/8/79	9/8/79	9/10/79	9/11/79	9/12/79	9/13/79	9/15/79	9/16/79	9/17/79
Onstream hours	33	24	24	14	38	26	24	29	16	44	24	24
Percent SO_2 removal	79.9	84.6	78.7	75.8	78.6	73.9	74.8	75.7	81.6	83.7	81.6	85.6
Inlet SO_2 concentration, ppm	1858	1618	2065	2025	2226	2093	1998	2474	2292	1912	1767	2125
SO_2 make-per-pass, m-moles/l	7.9	7.3	8.6	8.1	9.3	8.2	7.9	9.9	9.9	8.5	7.7	9.7
Inlet liquor $SO_3^=$ concentration, ppm	722	7	174	669	366	470	158	249	285	122	100	226
Inlet liquor percent gypsum saturation	130	95	125	125	130	105	120	110	115	110	110	105
Slurry percent solids	15.0	14.9	14.8	15.9	14.1	14.8	13.2	15.0	13.8	15.7	14.6	9.0
Percent sulfite oxidation	98.0	99.7	98.5	99.2	98.0	98.1	76.2	74.7	75.1	99.0	98.4	69.5
Percent limestone utilization	44	81	44	36	60	60	68	62	66	73	75	21
Inlet pH	5.20	5.40	5.05	5.10	5.25	5.00	5.25	5.25	5.45	5.35	5.35	5.65
Filter cake solids, wt %	83	86	80	85	82	86	--	71	70	87	82	-
Air stoichiometry, atoms O/mole SO_2 abs.	1.30	1.70	1.50	1.85	2.30	2.10	2.05	2.55	2.30	1.50	2.10	2.35
Mist eliminator restriction, %	-	-	-	-	-	-	-	-	-	-	-	-

(1) pH underride of 5.2
(2) Run with air stoichiometry control
(3) External downcomer for oxidation tank was used

Table 19-1 (continued)

RESULTS OF TCA LIMESTONE TESTS WITH FORCED OXIDATION USING ONE TANK - EFFECT OF AIR STOICHIOMETRY AND AGITATOR SPEED

Major Test Conditions	905-2A	905-2B	905-2C	905-2D	905-2E	905-2F	905-2G	905-2H	905-2I
Fly ash loading	High	High	High	High	High	High	High	High	High
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Liquor rate, gpm	1200	1200	1200	1200	1200	1200	1200	1200	1200
Percent solids recirculated	15	15	15	15	15	15	15	15	15
Limestone stoich. ratio(1) (controlled)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Oxidation tank residence time, min.	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
Tank level, ft.	17	17	17	17	17	17	17	17	17
Air rate to oxidizer, scfm(2)	0	53	67	87	116	117	128	148	172
Oxidizer Agitator Speed, rpm	54	54	54	54	54	36	36	36	36
Run-Average Results									
Start-of-Run Date	9/18/79	9/19/79	9/20/79	9/21/79	9/22/79	9/23/79	9/24/79	9/25/79	9/26/79
Onstream hours	20	20	24	24	24	23	24	24	24
Percent SO_2 removal	73.2	73.3	75.9	73.0	74.6	77.5	77.6	77.6	78.0
Inlet SO_2 concentration, ppm	2403	2545	2510	2280	2249	2226	2184	2238	2326
SO_2 make-per-pass, m-moles/l	9.3	9.9	10.1	8.8	8.9	9.2	9.0	9.2	9.6
Inlet liquor $SO_3^=$ concentration, ppm	36	231	222	72	602	190	240	150	172
Inlet liquor percent gypsum saturation	130	115	120	130	115	115	110	110	105
Slurry percent solids	15.3	15.8	16.1	14.3	15.0	14.9	16.0	15.4	15.1
Percent sulfite oxidation	35	55	59	62	85	67	69	66	65
Percent limestone utilization	83	80	78	80	69	83	86	83	81
Inlet pH	5.40	5.25	5.35	5.30	5.25	5.45	5.55	5.40	5.45
Filter cake solids, wt %	59	64	64	78	74	68	67	70	68
Air stoichiometry, atoms O/mole SO_2 abs.	0	0.60	0.72	1.06	1.45	1.40	1.55	1.75	1.95
Mist eliminator restriction, %	-	-	-	-	-	-	-	-	-

(1) pH underride of 5.2
(2) Run with air stoichiometry control

the initial runs, the resulting air stoichiometry was often excessively high with the accompanying high sulfite oxidation. Therefore, beginning from Run 904-2H, the air flow rate was varied to maintain a constant air stoichiometric ratio.

The effect of air stoichiometry and oxidation tank agitator speed on sulfite oxidation is plotted on Figure 19-1. Some scatter of data is observed. Four runs are not included in the plot: Runs 904-2F and 904-2G with air stoichiometries greater than 3, and Runs 904-2H and 904-2I with abnormally low inlet SO_2 concentrations (high expected natural oxidation level). In general, however, greater than 97 percent oxidation was achieved with an air stoichiometry higher than about 1.25 at 54 rpm agitator speed, and about 2.0 at 36 rpm, and about 2.5 at 18 rpm. Oxidation dropped off sharply with air stoichiometry lower than these levels.

High liquor sulfite accompanied by low limestone utilization (36 to 69 percent) was observed for 7 runs (Runs 904-2D, 904-2J, 904-2L, 904-2M, 904-2N, 904-2O, and 905-2E). These are indicated by the darkened symbols in Figure 19-1. Similar phenomena (high sulfite supersaturation and limestone blinding) had been experienced during limestone/adipic acid tests with forced oxidation using one tank (Section 17).

Low limestone utilization was observed for most of the runs conducted at 18 rpm agitator speed (Runs 904-2P, 904-2Q, 904-2R, and 904-2U). Limestone utilization for these runs ranged from 21 to 68 percent with 70 to 76 percent oxidation. Poor agitation with the lower agitator speed probably resulted in slower limestone dissolution rate. Limestone blinding by $CaSO_3$ was not the cause because sulfite oxidation was low (sufficient $CaSO_3$ solid crystals for sulfite desupersaturation) and the liquor sulfite concentration ranged only from 160 to 285 ppm.

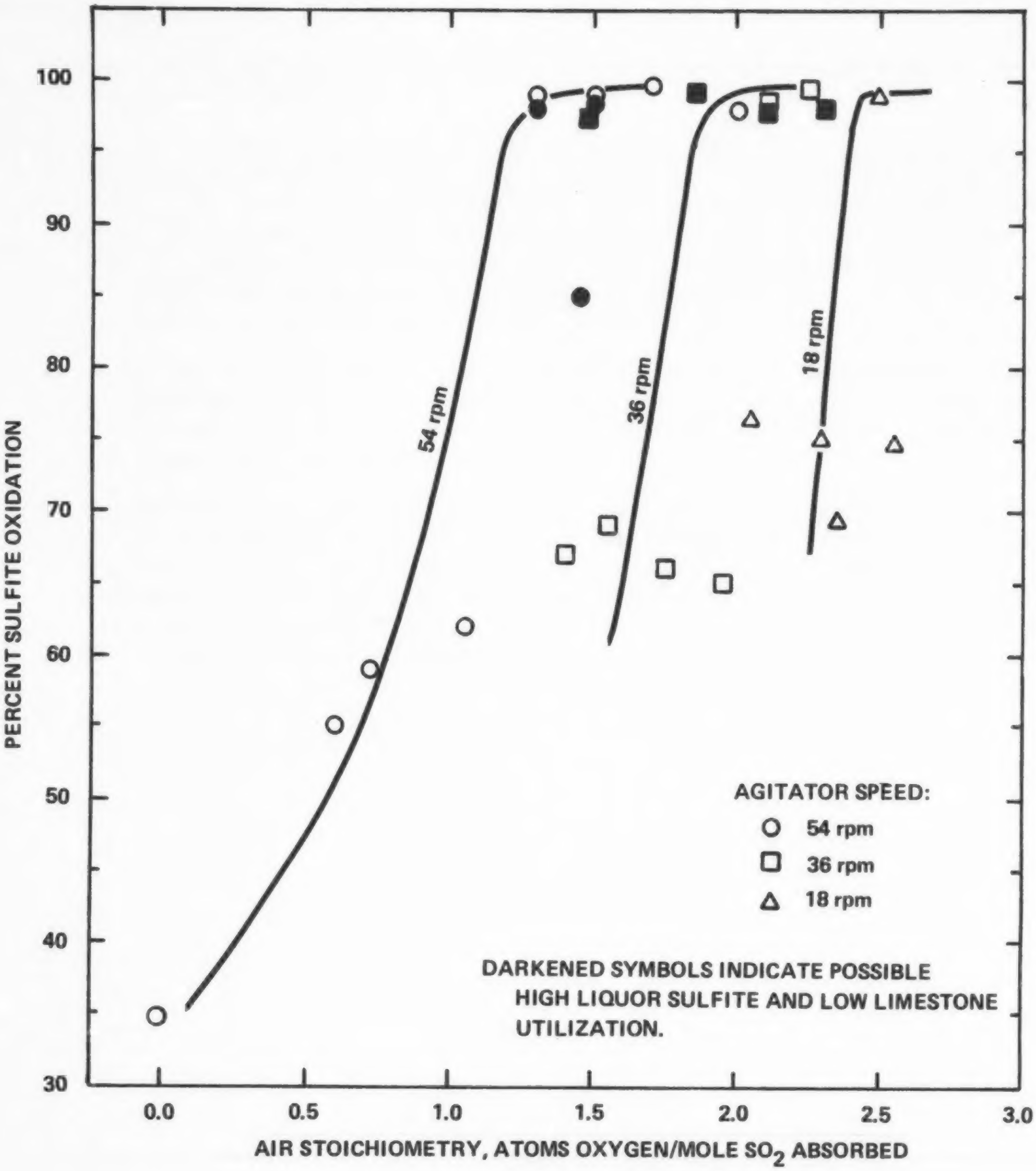

Figure 19-1

Effect Of Air Stoichiometry And Agitator Speed On Sulfite Oxidation

The following is a summary of the results of TCA limestone tests with in-loop forced oxidation using one tank:

- The oxidation tank agitator speed had a strong effect on the required air stoichiometry.

- With a 17-ft slurry level in the oxidation tank (7-ft tank diameter), 4.1 minutes residence time, and a controlled limestone stoichiometry of 1.2 moles Ca/mole SO_2 absorbed (TCA inlet pH 5.25 to 5.55 without limestone blinding), the required air stoichiometries to obtain greater than 97 percent oxidation were 1.25, 2.0, and 2.5 atoms oxygen/mole SO_2 absorbed with corresponding agitator speeds of 54, 36, and 18 rpm, respectively, for the two-turbine agitator.

- Limestone blinding by calcium sulfite (high liquor sulfite/low limestone utilization) could occur under the conditions given above. This phenomenon could be eliminated by using a higher air stoichiometry to reduce the liquor sulfite concentration.

- It should be possible to operate the oxidation tank without an agitator to achieve good oxidation. However, higher air stoichiometry (probably greater than 3.0) with a tank level of at least 17 ft would be needed to compensate for the drop in oxygen transfer efficiency. Whether the oxidized slurry solids can be kept in suspension without the agitator is not considered or addressed here.

Section 20

SIMULATION OF SPRINGFIELD FULL-SCALE ADIPIC ACID-ENHANCED LIMESTONE SCRUBBING ON THE TCA SYSTEM

As part of EPA's continuing program of FGD technology transfer, and to further demonstrate the effectiveness of adipic acid and encourage its use, EPA contracted with Radian Corporation in the spring of 1980 to conduct a full-scale demonstration program of adipic acid-enhanced limestone scrubbing. The program is being conducted with two 100-MW TCA's located at the Springfield City Utilities' Southwest Station near Springfield, Missouri. This station burns an eastern coal containing 3.5 percent sulfur. The TCA's treat fly ash-free flue gas from electrostatic precipitators.

The test program at Springfield includes both natural oxidation and forced oxidation in a limestone/adipic acid system using one scrubber loop and one tank.

Initial tests at Springfield without forced oxidation were conducted in August and September 1980 (Reference 21). Results from these tests were consistent with Shawnee findings. SO_2 removals fell within 1 to 3 percentage points of model prediction based on the Shawnee data under similar operating conditions. The fact that a different type of limestone was used at Springfield, (more coarsely ground), seemed to suggest that limestone type and grind might not be a strong factor in influencing the SO_2 removal efficiency when adipic acid is used.

It was noted that there was little noticeable odor associated with the adipic acid testing at Springfield.

Following these initial tests, the scrubber system was shut down for scheduled maintenance. Six months of testing at Springfield was scheduled to follow the January 1981 startup and system equilibration period. New online SO_2 and O_2 monitoring instruments are to be certified according to EPA certification procedures. The TCA system is being monitored for 3 months each in forced oxidation and natural oxidation modes.

To support the Springfield demonstration and to generate information useful for the planned full-scale operation, a four month Springfield simulation testing was conducted on the Shawnee TCA beginning in mid-July 1980.

It should be noted that a precise simulation of the Springfield operation with the Shawnee hardware was not possible. For example, because of the difference in the effluent hold tank designs (rectangular tank at Springfield vs. cylindrical tank at Shawnee), Shawnee could simulate either the effluent hold tank (oxidation tank) residence time or the tank level at Springfield, but not both. Therefore, emphasis during the simulation testing was placed more on the chemistry and the process than on the equipment.

20.1 SYSTEM DESCRIPTION

Eight runs were conducted from mid-July through mid-September 1980 with limestone/adipic acid without forced oxidation. The flow configuration for these runs is shown in Figure 20-1. Adipic acid was added either to the fresh limestone feed tank or directly to the effluent hold tank. The effluent hold tank is 20 ft in diameter.

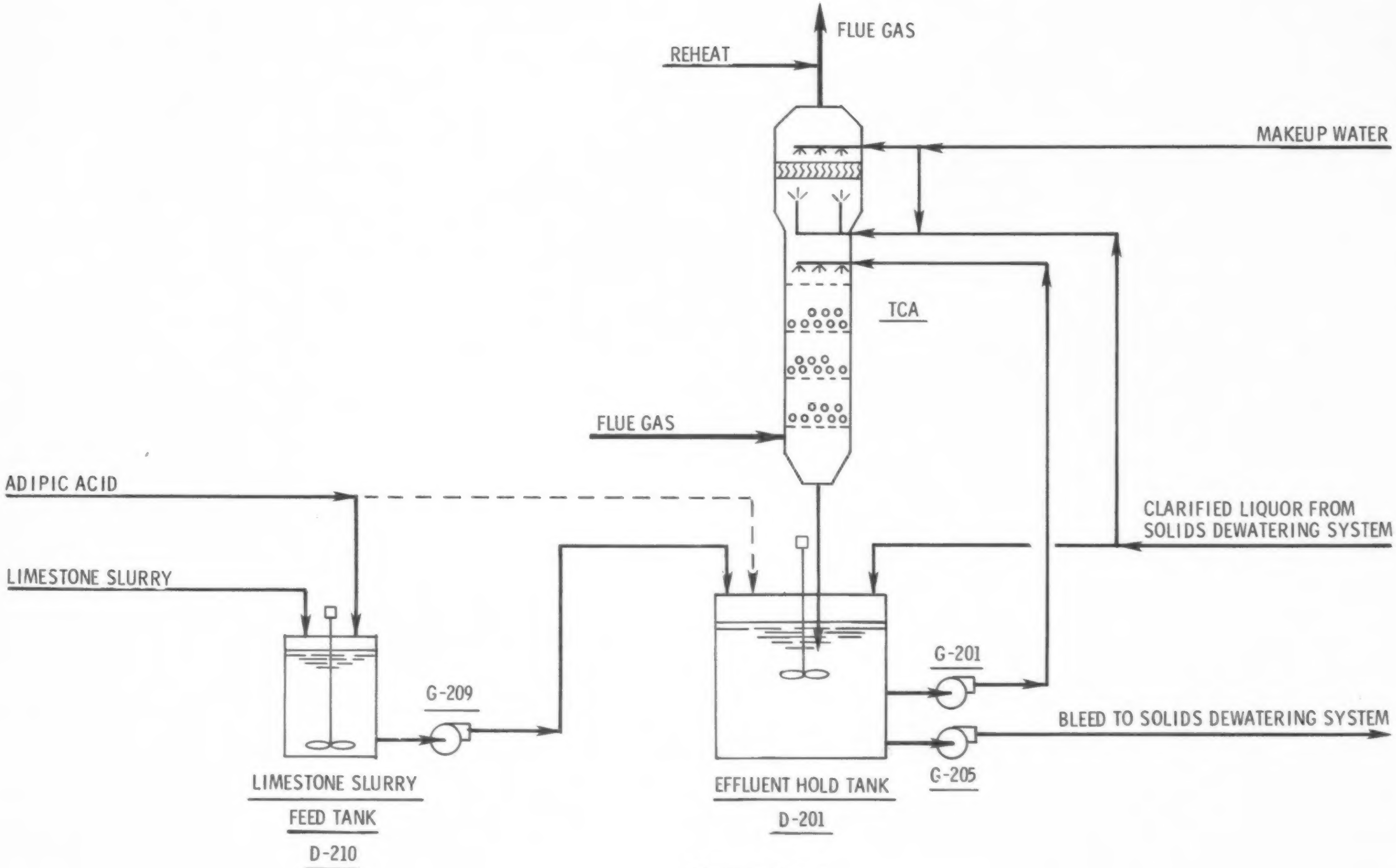
FLUE GAS
REHEAT
MAKEUP WATER
TCA
FLUE GAS
CLARIFIED LIQUOR FROM
SOLIDS DEWATERING SYSTEM
ADIPIC ACID
LIMESTONE SLURRY
G-209
G-201
G-205
BLEED TO SOLIDS DEWATERING SYSTEM
LIMESTONE SLURRY
FEED TANK
D-210
EFFLUENT HOLD TANK
D-201

Figure 20-1

Flow Diagram For The Springfield
Simulation On The TCA System Without
Forced Oxidation

Eleven runs were made from mid-September through mid-November 1980 with limestone/adipic acid with forced oxidation using a single tank. The flow diagram for these runs is given in Figure 20-2. Adipic acid was added to the fresh limestone feed tank in all 11 runs with forced oxidation. Air was injected into the 20 ft-diameter effluent hold tank (oxidation tank) through an air sparger. The air sparger was a five-prong "pitchfork" assembly of 3 and 4 inch-diameter 316L stainless steel pipe segments. On the underside of the pipe segments was a total of 40 holes, spaced about 2 ft apart. Each hole consisted of a 1/4-inch diameter by 3/4-inch long nipple welded onto the pipe segments. The agitator in the oxidation tank had a 20 Hp motor and was operated at 68 rpm. It had a 66-inch diameter downflow turbine containing 3 blades. Each blade had a stabilizing fin.

All tests, with or without forced oxidation, used three beds with 5 inches/bed of 38 mm diameter, 6 gram high density polyethylene spheres, similar to the type used at Springfield. Flue gas with low fly ash loading (0.2-0.6 grain/dry scf) was used in all runs.

20.2 DISCUSSION OF TEST RESULTS

The results of 8 runs (Runs 934-2A through 934-2H) with limestone/adipic acid and without forced oxidation are presented in Table 20-1. The results of 11 runs (Runs 907-2A through 907-2G and Runs 907-2J through 907-2M) with limestone/adipic acid and with one-tank forced oxidation are given in Table 20-2.

20.2.1 Tests without Forced Oxidation

Common test conditions for the 8 runs without forced oxidation were (see Table 20-1):

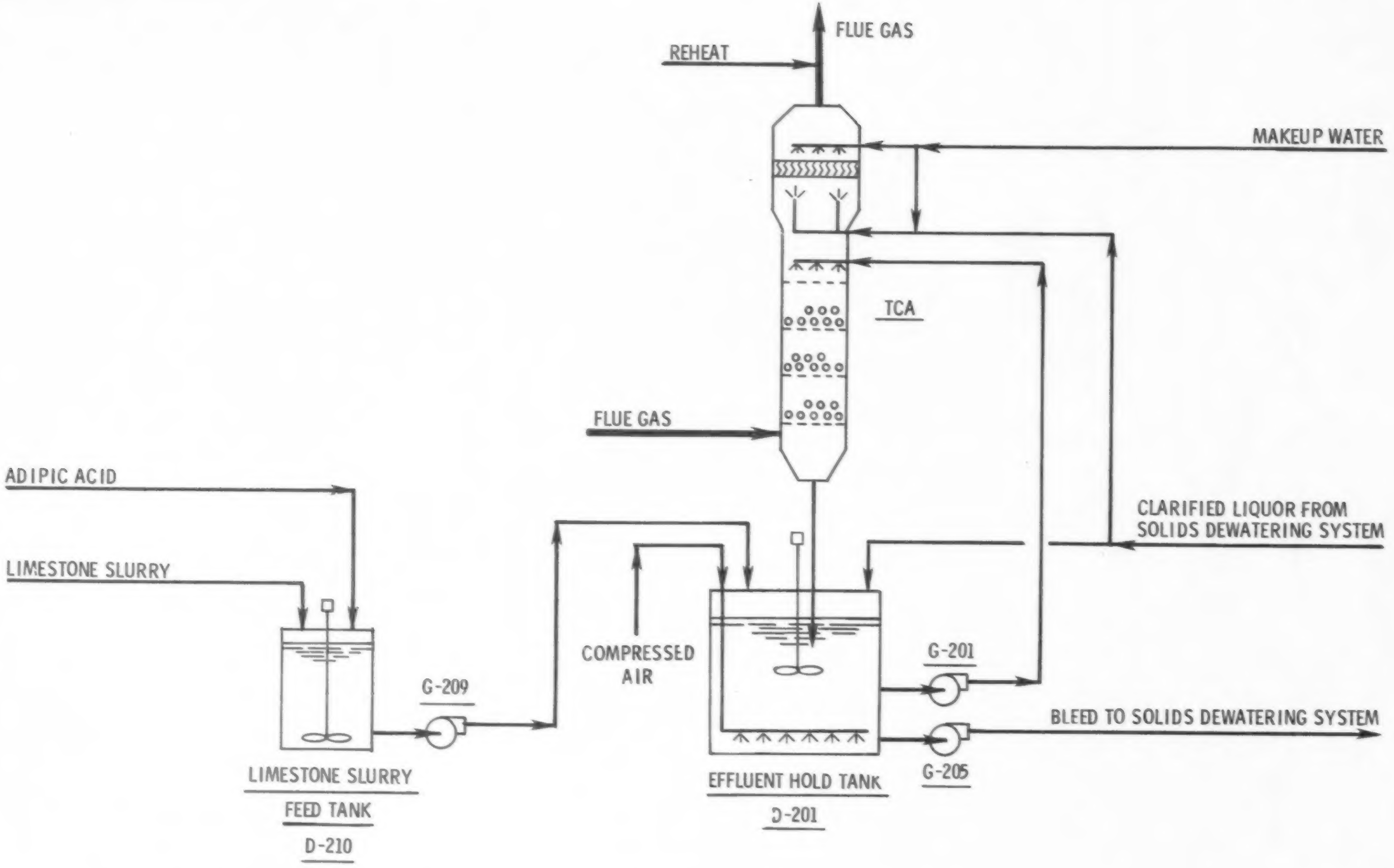
FLUE GAS
REHEAT
MAKEUP WATER
TCA
FLUE GAS
ADIPIC ACID
LIMESTONE SLURRY
CLARIFIED LIQUOR FROM
SOLIDS DEWATERING SYSTEM
COMPRESSED
AIR
G-201
G-209
BLEED TO SOLIDS DEWATERING SYSTEM
G-205
LIMESTONE SLURRY
FEED TANK
D-210
EFFLUENT HOLD TANK
D-201

Figure 20-2

Flow Diagram For The Springfield Simulation
On The TCA System With Forced Oxidation

Table 20-1

RESULTS OF TCA LIMESTONE/ADIPIC ACID TESTS
WITHOUT FORCED OXIDATION
(SPRINGFIELD SIMULATION)

Major Test Conditions (1)	934-2C	934-2A	934-2B	934-2E	934-2F	934-2D	934-2G	934-2H
Fly ash loading	Low	Low	Low	Low	Low	Low	Low	Low
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Slurry rate, gpm	1200	1200	1200	1200	1200	1200	900	900
Slurry solids concentration wt% (controlled)	10	10	10	10	10	10	10	10
Scrubber inlet pH (controlled)	5.4	4.6	5.0	5.0	4.6	5.4	5.0	5.1
Adipic acid addition point	EHT	EHT	EHT	Limestone Tank	Limestone Tank	Limestone Tank	Limestone Tank	Limestone Tank
Adipic acid concentration, ppm	1500	1500	1500	1500	1500	1500	1500	2500
EHT residence time, min.	37.2	37.2	37.2	37.2	37.2	37.2	50	50
Dewatering system	Clarifier & Belt Filter	Clarifier & Belt Filter	Clarifier & Drum Filter	Clarifier & Drum Filter	Clarifier & Belt Filter	Clarifier & Belt Filter	Clarifier & Belt Filter	Clarifier & Belt Filter
Run-Average Results								
Start-of-run date	7/18/80	7/31/80	8/5/80	8/9/80	8/14/80	8/20/80	8/27/80	9/2/80
Onstream hours	296	123	85	95	136	168	145	192
Percent SO_2 removal	92.9	59.2	91.7	78.0	43.9	94.7	64.9	78.3
Inlet SO_2 concentration, ppm	2100	2350	2300	2410	2275	2344	2350	2120
Adipic acid concentration, ppm	1500	1550	1480	1540	1525	1565	1575	2475
Actual adipic acid consumption, lbs/ton SO_2 absorbed	21.7	3.54	9.00	11.0	7.89	11.1	6.6	8.8
Adipic acid consumption ratio (actual/theor.)	10.5	2.0	3.5	3.7	6.7	4.3	3.6	2.7
Slurry solids concentration wt% (controlled)	10.8	9.7	9.7	9.9	9.3	9.9	9.6	10.3
Scrubber inlet pH	5.35	4.55	4.95	5.00	4.59	5.40	5.05	5.05
Scrubber outlet pH	4.80	4.00	4.27	4.24	4.00	4.7	4.00	4.23
SO_2 make-per-pass, mmole/l	10.4	7.3	9.9	10.1	5.3	11.8	10.3	11.8
Limestone utilization, %	96.7	98.9	98.5	98.0	98.2	96.0	98	97
Scrubber inlet sulfite concentration, ppm	490	2668	1196	1329	3044	643	1450	1285
Scrubber outlet sulfite concentration, ppm	1135	3268	2139	2429	3874	1562	2590	2710
Sulfite oxidation, %	41.5	57.3	40.3	38.3	50.3	23.2	26.9	25.1
Filter cake solids, wt %	78	85	73	71	87	74	80	77.7
Total pressure drop, inches H_2O	8.1	7.9	7.6	7.6	8.2	8.6	6.5	6.6
Mist eliminator restriction, %	--	--	--	--	--	--	-	<3
Scrubber inlet gypsum saturation, %	100.0	95.1	101.2	107.5	104.1	103.0	98.3	104.0

(1) All runs were made using three beds (4 grids) with nominally 5 inch/bed of 38mm diameter high density polyethylene spheres, and with a 19 ft tank level.

Table 20-2

RESULTS OF TCA LIMESTONE/ADIPIC ACID TESTS WITH ONE TANK AND FORCED OXIDATION (SPRINGFIELD SIMULATION)

Major Test Conditions (1)	907-2A	907-2B	907-2C	907-2D	907-2E	907-2F	907-2G	907-2J	907-2K	907-2L	907-2M
Fly ash loading	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low
Gas rate, acfm @ 300°F	30,000	30,000	30,000	30,000	25,000	20,000	20,000	30,000	30,000	30,000	30,000
Slurry rate, gpm	1,200	1,200	1,200	1,200	1,200	1,200	600	1,200	1,200	1,200	1,200
Slurry solids concentration, wt% (controlled)	10	10	10	10	10	10	10	10	10	10	10
Inlet liquor pH (controlled)	4.8	4.8	4.8	4.8	4.8	4.8	4.8	5.0	5.0	5.2	5.2
Adipic acid addition point	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank	Limestone Feed Tank
Adipic acid concentration, ppm	2,500	2,500	2,500	2,500	2,500	2,500	2,500	2,000	2,000	1,600	1,600
EHT residence time, min	35	29	22	22	22	22	43	29	35	35	29
EHT level, ft	18	15	11	11	11	11	11	15	18	18	15
Air rate, scfm	250	250	250	350	350	350	350	250	250	250	250
Run-Average Results											
Start-of-run date	9/11/80	9/22/80	9/25/80	10/4/80	10/10/80	10/16/80	10/21/80	10/27/80	11/3/80	11/7/80	11/13/80
Onstream hours	221	71	124	142	144	120	136	162	88	148	84
Percent SO_2 removal	95.3	96.5	93.0	96.4	93.9	95.3	70.6	97.6	97.2	98.0	94.7
Inlet SO_2 concentration, ppm (2)	2835	2570	2620	2520	2530	2450	2355	2355	2255	2450	2435
Adipic acid concentration, ppm	2485	2700	2545	2675	2710	2450	2510	2005	2060	1740	1590
Adipic acid consumption, lbs/ton SO_2 absorbed	30.7	11.2	21.6	11.5	2.33	7.41	9.3	19.51	14.6	20.1	7.42
Adipic acid consumption ratio (actual/theor.)	17.5	7.6	7.7	4.5	1.24	3.85	7.8	21.90	13.7	15.5	2.2
Slurry solids concentration, wt% (controlled)	10.0	10.1	10.1	10.0	9.9	9.9	9.9	10.2	10.0	9.8	9.8
Scrubber inlet pH	4.75	4.80	4.75	4.85	4.81	4.81	4.82	4.98	5.00	5.15	5.30
Scrubber outlet pH	4.35	4.55	4.45	4.45	4.36	4.37	4.39	4.55	4.34	4.41	4.80
SO_2 make-per-pass, m moles/l	14.3	13.1	12.9	12.9	10.5	8.2	11.7	12.2	11.6	12.7	12.2
Limestone utilization, %	91	91	50	66	76.9	89.3	95.2	81.3	96.6	90.9	47.6
Scrubber inlet sulfite concentration, ppm	290	180	830	105	40	120	55	290	95	185	1525
Scrubber outlet sulfite concentration, ppm	1200	875	1670	995	781	715	1259	500	260	725	1945
Sulfite oxidation, %	99.8	98.4	99.1	99.9	99.9	99.7	99.9	99.8	99.9	99.9	91.0
Filter cake solids, wt %	89	91	88	87	90	88	92	93	91	88	80
Scrubber inlet gypsum saturation, %	101	100	111	110	104	113	112	121	117	120	130
Total pressure drop, inches H_2O	10.6	9.1	7.90	8.3	6.0	4.3	3.4	10.6	10.0	11.7	10.1
Mist eliminator restriction, %	-	-	-	-	-	-	10	-	-	-	21
Air Stoich, Atoms O/moles SO_2 absorbed	1.9	2.1	2.1	2.9	3.6	4.6	6.5	2.2	2.3	2.1	2.2

(1) All runs were made using three beds (4 grids) with nominally 5 inches/bed of 38mm diameter high density polyethylene spheres.

(2) The SO_2 inlet concentrations presented here from 10:00 am October 9, 1980, through 11:00 am October 31, 1980, has been increased 360 ppm to compensate for a leak that was discovered in the SO_2 inlet meter.

Fly ash loading: Low (0.2 to 0.6 grain/dry scf)
Gas rate: 30,000 acfm @ 300°F
Slurry solids concentration: 10 percent
Solids dewatering system: Clarifier and filter
Total static bed height: 15 inches of 38mm diameter, 6 gram HDPE spheres
Slurry level in EHT: 19 ft

A slurry level of 19 ft in the effluent hold tank was used to approximate the 23 ft level at Springfield. This resulted in a high residence time of 37 minutes at 1200 gpm slurry flow rate compared to about 15 minutes at Springfield.

Effect of Adipic Acid Feed Location. Six runs (Runs 934-2A through 934-2F) were made to investigate the effect of adipic acid feed location (EHT vs. fresh limetone feed tank) on the TCA performance and adipic acid consumption. It was expected that the acid feed point at Springfield would be in the fresh limestone feed tank rather than in the effluent hold tank typical of Shawnee operation. All six runs were made with 1500 ppm adipic acid and 1200 gpm slurry flow rate (L/G = 50 gal/mcf). Feed location (see Figure 20-1) was varied at three scrubber inlet pH levels of 4.6, 5.0, and 5.4.

Within the accuracy of material balance calculations, there was no convincing evidence indicating that the adipic acid feed location had an effect on the acid consumption rate or other system performance.

The high adipic acid consumption rate of 21.7 lb/ton SO_2 absorbed for Run 934-2C was probably due to unsteady-state buildup of adipic acid to the desired concentration of 1500 ppm.

With the exception of Run 934-2C, the actual-to-theoretical adipic acid consumption ratio for the first six runs in Table 20-1 varied from 2.0 to 6.7 when operating within the pH range of 4.6 to 5.4 at the scrubber inlet. These values are all considerably greater than those in previous Shawnee tests without forced oxidation when flue gas with high fly ash loading was used. Tests with low fly ash loading in this series resulted in significantly tighter liquor loop closure because of decreased rates of waste solids (containing low fly ash loading) and the associated liquid discharged from the system. This nearly doubled the adipic acid retention time in the system (scrubber and dewatering areas), and consequently caused higher adipic acid degradation.

Note that the actual-to-theoretical adipic acid consumption ratio is a measure of the degree of degradation. With the tight liquor loop closure in these runs, the actual adipic acid consumption was no greater than that in runs with high fly ash loading (see, for example, Table 7-1), even though the consumption ratios were higher. Except for Run 934-2C, the actual consumption for the six runs varied from 3.54 to 11.1 lb/ton SO_2 absorbed, or 2.2 to 6.8 lb/ton limestone, at 4.6 to 5.4 scrubber inlet pH.

At 1500 ppm nominal adipic acid concentration, SO_2 removal was sensitive to scrubber inlet pH, as would be expected. For Runs 934-2A through 934-2F, SO_2 removal varied from 43.9 percent at a scrubber inlet pH of 4.6 to 94.7 percent at 5.4 inlet pH. There was no evidence that the adipic acid feed location affected SO_2 removal.

Limestone utilization was high for all runs, ranging from 96.0 to 98.9 percent at 4.6 to 5.4 scrubber inlet pH with the high effluent hold tank residence time of 37 minutes.

Sulfite oxidation varied from a low of 23 percent at 5.4 scrubber inlet pH to a high of 57 percent at 4.6 inlet pH.

Effect of Slurry Flow Rate. Run 934-2G (see Table 20-1) was conducted at a reduced slurry flow rate of 900 gpm and 50 minutes residence time, to compare with Run 934-2E which was made at 1200 gpm slurry flow rate and 37 minutes residence time. Other test conditions were the same for the two runs. Predictably, SO_2 removal decreased from 78.0 to 64.9 percent. Limestone utilization for both runs was 98 percent. There was no significant difference in the adipic acid consumption ratio, which was 3.7 for Run 934-2E and 3.6 for Run 934-2G. The actual adipic acid consumption was much higher for Run 934-2E at 11.0 lb/ton SO_2 absorbed, compared to 6.6 lb/ton SO_2 absorbed for Run 934-2G. This may have been caused partly by the tighter liquor loop closure during Run 934-2G with 80 percent filter cake solids using the belt filter, compared to 71 percent cake solids for Run 934-2E using the drum filter.

Effect of Adipic Acid Concentration. In Run 934-2H, the adipic acid concentration was raised to 2500 ppm with other conditions held the same as for Run 934-2G. As expected, SO_2 removal increased from 64.9 to 78.3 percent. The adipic acid consumption ratio was lower at 2.7 and limestone utilization was essentially unchanged at 97 percent.

At the end of Run 934-2H, an inspection showed that about half of the HDPE spheres had failed. Some of the failed spheres were filled with slurry, rendering them immobile. Most of the failed spheres were replaced with available new ones (about 10,500) before Run 907-2A (see Table 20-2) was started. The service time for these spheres totaled 1240 hours during Runs 934-2A through 934-2H. This was significantly lower than about 2000 hours of service life experienced at Shawnee (Reference 21).

20.2.2 Tests with Forced Oxidation Using One Tank

Common test conditions for the 11 runs with forced oxidation were (see Table (20-2):

Fly ash loading:	Low (0.2 to 0.6 grain/dry scf)
Slurry solids concentration:	10 percent
Adipic acid addition point :	Limestone feed tank
Solids dewatering system:	Clarifier and filter
Total static bed height:	15 inches of 38mm diameter, 6 gram HDPE spheres

The major objective of the 11 runs was to define the ranges of operating parameters in which limestone blinding by calcium sulfite would not occur.

Effect of Oxidation Tank Level. Runs 907-2A, 907-2B, and 907-2C were made under the same operating conditions except that the oxidation tank level was varied at 18, 15, and 11 ft, respectively. The corresponding oxidation tank residence times were 35, 29, and 22 minutes. For these runs, the scrubber inlet pH was held constant at 4.8, adipic acid concentration at 2500 ppm, and air rate at 250 scfm. The gas rate was 30,000 acfm at 300°F and the slurry flow rate was 1200 gpm (L/G = 50 gal/mcf).

Limestone blinding did not occur until the tank level was dropped to 11 ft in Run 907-2C. Limestone utilization was 91 percent in both Runs 907-2A and 907-2B, and dropped to only 50 percent in Run 907-2C. Scrubber inlet liquor sulfite concentration increased concurrently from 290 and 180 ppm for Runs 907-2A and 907-2B to 830 ppm for Run 907-2C. Apparently, the 11 ft tank level did not provide sufficient air bubble residence times to give a good liquid phase oxidation intensity. As a result, sulfite built up in the liquor causing supersaturation and limestone blinding in the slurry which was deficient in $CaSO_3$ solid seed crystals.

SO_2 removals for Runs 907-2A, 907-2B, and 907-2C were high, ranging from 93.0 to 96.5 percent with average inlet SO_2 concentrations of 2570 to 2835 ppm. Sulfite oxidation was high, ranging from 98.4 to 99.8 percent.

At the end of Run 907-2A, all high density polyethylene spheres in the TCA were replaced with new ones.

The effect of the oxidation tank level was also investigated at a higher scrubber inlet pH of 5.0 and 5.2 during Runs 907-2J through 907-2M.

Runs 907-2J and 907-2K were made at a scrubber inlet pH of 5.0 and an adipic acid concentration of 2000 ppm, with 15-ft and 18-ft tank levels, respectively. All other conditions were the same as those for Runs 907-2A through 907-2C. Some limestone blinding was apparent during Run 907-2J with 81.3 percent limestone utilization at 15-ft tank level, as compared to 96.6 percent limestone utilization for Run 907-2K at 18-ft tank level. SO_2 removal was 97.6 and 97.2 percent, and sulfite oxidation was 99.8 and 99.9 for Runs 907-2J and 907-2K, respectively.

In Runs 907-2L and 907-2M, the scrubber inlet pH was controlled at 5.2 and adipic acid concentration at 1600 ppm, with 18-ft and 15-ft tank levels, respectively. All other conditions were unchanged. Limestone blinding was severe in Run 907-2M at 15-ft tank level, giving a limestone utilization of only 47.6 percent, as compared to 90.9 percent for Run 907-2L with an 18-ft tank level. Thus, higher pH gives a higher limestone blinding tendency, as would be expected from increased sulfite saturation. SO_2 removal was 98.0 and 94.7 percent, and sulfite oxidation was 99.9 and 91.0 percent for Runs 907-2L and 907-2M, respectively. The low 91.0 percent oxidation was the combined result of high pH (5.3) and low tank level (15 ft).

Effect of Air Stoichiometry. In Run 907-2D, air flow rate to the oxidizer was raised from 250 to 350 scfm to observe whether the higher oxidation intensity with the higher air rate could eliminate limestone blinding and improve the limestone utilization. Other test conditions for Run 907-2D were the same as for Run 907-2C.

Air stoichiometry increased from 2.1 to 2.9 atoms oxygen/mole SO_2 absorbed. The limestone utilization improved from 50 to 66 percent, indicating that the limestone blinding still existed at the low 11-ft tank level. Unfortunately, the air flow rate could not be increased further because of the limitation on the compressor capacity.

SO_2 removal increased from 93.0 percent for Run 907-2C to 96.4 percent for Run 907-2D, probably because of reduced bisulfite concentration (sulfite/bisulfite concentration, expressed as $SO_3^{=}$, decreased from 830 to 105 ppm) with more vigorous oxidation. This was reflected in the increased oxidation in solids from 99.1 to 99.9 percent.

Effect of Reduced Gas Rate. Because of the limited air compressor capacity, the air stoichiometry was raised indirectly by reducing the gas rate from 30,000 acfm in Run 907-2D to 25,000 acfm in Run 907-2E, and further to 20,000 acfm in Run 907-2F. Other test conditions were held the same as in Run 907-2D. Increasing the air stoichiometry should eventually eliminate the limestone blinding problem.

The air stoichiometry increased from 2.9 to 3.6, and to 4.6 atoms oxygen/mole SO_2 absorbed. Limestone utilization did improve from 66 to 76.9, and further to 89.3 percent for Runs 907-2D, 907-2E, and 907-2F, respectively. Sulfite oxidation remained high at 99.9 and 99.7 percent for Runs 907-2E and 907-2F. SO_2 removal for the three runs varied from 93.9 to 96.4 percent.

Thus, at an 11-ft tank level, air stoichiometry as high as 4.6 atoms oxygen/mole SO_2 absorbed did not completely eliminate the limestone blinding, giving 89.3 percent limestone utilization in Run 907-2F.

Effect of Reduced Slurry Flow Rate. In Run 907-2G, the slurry flow rate was reduced from 1200 to 600 gpm with other conditions the same as Run 907-2F. This effectively doubled the oxidation tank residence time from 22 to 43 minutes at the same 11-ft tank level.

Limestone utilization improved to 95.2 percent, suggesting that the limestone blinding had essentially been eliminated. The improved limestone utilization was a combined result of the higher residence time and a higher air stoichiometry of 6.5 atoms oxygen/mole SO_2 absorbed. The reduced slurry flow rate of 600 gpm dropped the SO_2 removal to only 70.6 percent which in turn increased the air stoichiometry. Sulfite oxidation remained excellent at 99.9 percent.

20.3 SUMMARY

20.3.1 Tests without Forced Oxidation

Runs 934-2A through 934-2H (Table 20-1) were made without forced oxidation. All eight runs were made with 19-ft slurry level in the effluent hold tank, resulting in 37 minutes residence time at 1200 gpm slurry flow rate and 50 minutes at 900 gpm, as compared to 23-ft tank level and about 15 minutes residence time at 13,000 gpm at Springfield. High density polyethylene spheres were used as in Springfield. A summary of major test results follows:

- At about 1500 ppm adipic acid and an L/G of 50 gal/mcf (30,000 acfm and 1200 gpm), average SO_2 removal was 93 to 95 percent at 5.4 scrubber inlet pH, 78 to 82 percent at 5.0 pH, and 44 to 59 percent at 4.6 pH (Runs 934-2A through 934-2F). Average inlet SO_2 concentration varied from 2100 to 2400 ppm.

- At an L/G of 37 gal/mcf (30,000 acfm and 900 gpm) and a scrubber inlet pH of 5.1, average SO_2 removal was 65 percent at 1600 ppm adipic acid (Run 934-2G) and 78 percent at 2500 ppm adipic acid (Run 934-2H). These SO_2 removal values may have been low because half of the spheres had failed at the end of Run 934-2H.

- Limestone utilization for all tests (4.6 to 5.4 inlet pH and 37 to 50 minutes residence time) averaged 96.0 to 98.9 percent.

- Within the accuracy of material balance calculations for adipic acid, there is no conclusive evidence as to whether the addition of adipic acid to the effluent hold tank or limestone feed tank had an effect on adipic acid consumption or scrubber performance (Runs 934-2A, 2B, and 2C versus Runs 934-2D, 2E, and 2F).

- With the exception of Runs 934-2C and 934-2F, the actual-to-theoretical adipic acid consumption ratio generally increased with increasing pH; the ratio was 2.0 at a scrubber inlet pH of 4.6, 2.7 to 3.7 at a pH of 5.0, and 4.3 at a pH of 5.4. These values are all higher than those in other Shawnee tests without forced oxidation. The difference may be a result of the low fly ash loading in the flue gas used in the Springfield simulation tests, which resulted in nearly twice the adipic acid retention time and higher degradation. However, the actual adipic acid consumptions of 3.5 to 11 lb/ton SO_2 absorbed (except Run 934-2C) are comparable to those for other Shawnee tests because of the tighter liquor loop operation (less liquor discharged with waste sludge because of low fly ash).

Recommendation: Without forced oxidation, it is recommended that the scrubber inlet pH be held at 4.8 to 5.0. The required adipic acid concentration would be about 2000 ppm to achieve greater than 90 percent SO_2 removal under the operating conditions at Springfield. Inlet pH lower than 4.8 is not recommended, because the level of natural oxidation could become sufficiently high to cause limestone blinding and the SO_2 removal is more sensitive to pH and inlet SO_2 variations at the lower pH. Inlet pH higher than 5.0, on the other hand, decreases the limestone utilization and increases the adipic acid degradation.

20.3.2 Tests with Forced Oxidation Using One Tank

A total of 11 runs were made with forced oxidation (see Table 20-2). Seven runs, Runs 907-2A through 907-2G, were all made at the same scrubber inlet pH of 4.8 and 2500 ppm adipic acid concentration, but with varying gas and liquor rates, oxidation tank level, and air flow rate, to observe the effect on limestone blinding tendency. Four runs, Runs 907-2J through 907-2M, were made with higher scrubber inlet pH of 5.0 and 5.2, and with varying oxidation tank levels and adipic acid concentrations to observe the effects of SO_2 removal as well as limestone blinding tendency. The following is a summary of major test results:

- Average SO_2 removal was 93 to 98 percent with inlet SO_2 concentrations of 2300 to 2800 ppm under the following sets of conditions:
    - L/G = 50 to 75 gal/mcf (20,000 to 30,000 acfm, 1200 gpm), inlet pH = 4.8, adipic acid concentration = 2500 ppm.
    - L/G = 50 gal/mcf (30,000 acfm, 1200 gpm), inlet pH = 5.0, adipic acid concentration = 2000 ppm
    - L/G = 50 gal/mcf (30,000 acfm, 1200 ppm), inlet pH = 5.2, adipic acid concentration = 1600 ppm
- Average SO_2 removal was only 71 percent at an L/G of 37 (20,000 acfm, 600 gpm), inlet pH of 4.8 and 2500 ppm adipic acid.
- Sulfite oxidation in solids averaged 98.4 to 99.9 percent with 1.9 to 6.5 air stoichiometry. An air stoichiometry of 2.0 is sufficient to obtain the high sulfite oxidation without regard to the limestone blinding possibility.
- At a scrubber inlet pH of 4.8 and an air stoichiometry of 2, limestone utilization was 91 percent with 15 and 18-ft oxidation tank levels (Runs 907-2A and 907-2B). Severe limestone blinding occurred when the tank level was dropped to 11 ft, giving a limestone utilization of only 50 percent (Run 907-2C). Limestone utilization improved to 66, 77, and 89 percent at an 11-ft tank level and 4.8 inlet pH when the air stoichiometry was increased to 2.9, 3.6, and 4.6, respectively, by increasing the air flow rate or decreasing the gas rate (Runs 907-2D, 2E, and 2F).
- At a scrubber inlet pH of 5.0 and an air stoichiometry of 2.2, slight limestone blinding occurred (81 percent limestone utilization) at a

15-ft tank level (Run 907-2J). Limestone blinding became severe (48 percent utilization) when the pH was increased to 5.2 with the same 15-ft tank level and 2.2 air stoichiometry (Run 907-2M).

- At a tank level of 18 ft, no limestone blinding occurred with 4.8 to 5.2 scrubber inlet pH and 1.9 to 2.3 air stoichiometry (Runs 907-2A, 907-2K, and 907-2L).
- Data on the adipic acid consumption ratio are too scattered to allow any conclusions. However, the general trends of increased adipic acid consumption (degradation) with increasing pH and with forced oxidation should still be valid. The scatter in the data of adipic acid consumption ratio is probably caused by the very high liquor loop closure (usually 87 to 93 percent solids in filter cake and low fly ash content), making the estimation of theoretical adipic acid consumption sensitive to the filter cake liquor content.

Recommendation: With forced oxidation, the recommended scrubber inlet pH is 4.8 to 5.0, as in the case without forced oxidation. Required adipic acid concentration for better than 90 percent SO_2 removal should be about 2000 ppm under the operating conditions at Springfield. At the recommended scrubber inlet pH of 4.8 to 5.0, an air stoichiometry of 1.9 to 2.3 atoms oxygen/mole SO_2 absorbed should give sufficient oxidation intensity in the slurry to prevent limestone blinding and to give good solids oxidation. The recommended minimum slurry level in the oxidation tank is 18 ft.

Section 21

TESTING WITH GLITSCH GRID PACKING ON TRAIN 200

At the conclusion of the Springfield simulation test series (Section 20), the high density polyethylene spheres in the TCA were removed and 4 ft in height of type 2-Z (316L stainless steel) Glitsch Grid packing (manufactured by Glitsch, Inc.) was installed between the second and third bar grids (middle bed). The purpose of this testing was to evaluate the pressure drop/flooding characteristics and the SO_2 removal efficiency of Glitsch Grid packing as an alternative packing for FGD scrubbers. All tests were made with limestone and without adipic acid.

21.1 PRESSURE DROP/FLOODING TESTS

Pressure drop tests began on November 24, 1980. For all these tests flue gas with high fly ash loading and limestone slurry with a solids concentration of about 15 percent were used.

Initial tests with 4-ft (23 layers) and 2-ft (12 layers) packing heights showed very high pressure drops across the packing. As a result, the packing height was further reduced to about 1 ft (7 layers).

At 1-ft packing height, a total of 64 tests (including repeats) were conducted at various gas and slurry flow rates. Nine levels of gas flow rates that correspond to 7.5 to 14.2 ft/sec gas velocity (cross section of scrubber was 32

ft^2) and five levels of slurry flow rates (600 to 1400 gpm) were tested. At each slurry flow rate the gas flow rate was adjusted from 18,000 to 34,000 acfm (300°F) at increments of 2000 acfm. Each set of test conditions was held for one hour and four sets of pressure drop data were taken within the hour.

Results of all 64 runs are graphically presented in Figure 21-1. Each point on the graph represents the average of four or more measurements. It is clear from the graph that the pressure drop across the Glitsch Grid packing increases with increasing gas velocity and slurry flow rate. No flooding appeared to occur up to the 34,000 acfm gas rate and 1400 gpm slurry flow rate tested.

21.2 RELIABILITY VERIFICATION RUN 935-2A

Run 935-2A with 1-ft Glitsch Grid packing started on December 2, 1980, after a scrubber internal inspection following the pressure drop/flooding tests. The packing was not cleaned prior to this run. There were two main objectives of this run. The first objective was to assess the reliability of Glitsch Grid packing with respect to scaling and plugging. The second objective was to evaluate the SO_2 removal efficiency of the packing and to compare the results with the performance of an earlier limestone test (Run 718-2A) made in 1977 using a Ceilcote fiberglass-filled-polypropylene egg-crate type packing (Reference 5). The results are also compared with a typical TCA limestone run with mobile spheres.

Run 935-2A was terminated on December 10, 1980, after a total of 128 onstream hours. For this test flue gas with high fly ash loading was utilized. The limestone stoichiometric ratio was controlled at 1.2 moles Ca/mole SO_2 absorbed. The slurry solids concentration was controlled at 15 percent. The flue gas flow rate of 30,000 acfm (at 300°F) and the slurry flow rate of 1200 gpm (L/G =

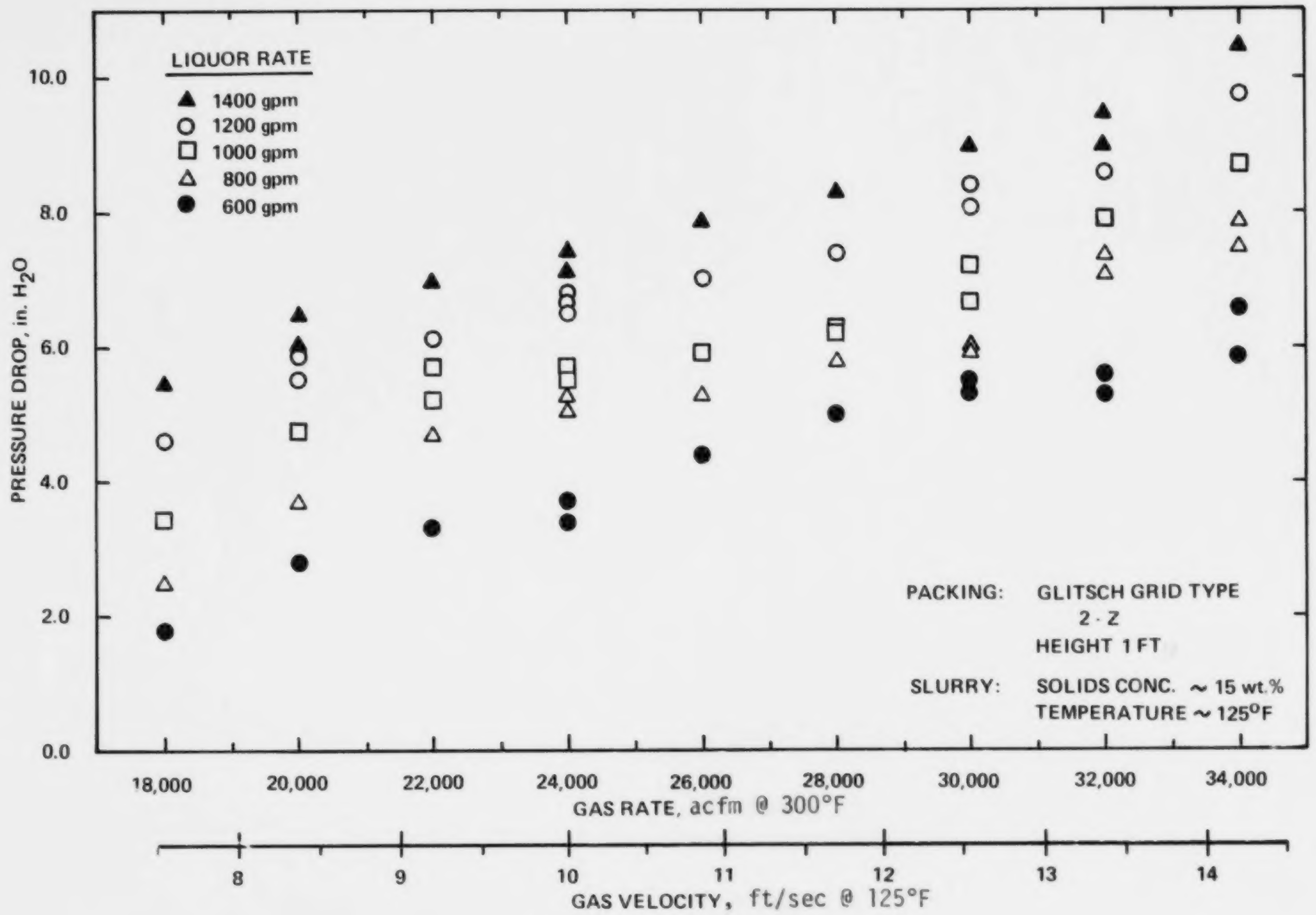

Figure 21-1

Pressure Drop Across Four Bar Grids And 1 ft Glitsch Grid Type 2-Z Packing

50 gal/mcf) were held constant. The packing was inspected at the end of the run after a total of 235 hours without cleaning (128 hours for Run 935-2A plus 107 hours for pressure drop tests). Judging from the extent of scale and solids accumulation in 235 hours of operation, the packing probably would not be suitable for long-term reliable service in a limestone slurry scrubber.

The results of Run 935-2A are compared in Table 21-1 with the earlier Run 718-2A using Ceilcote egg-crate type packing, which was made under similar operating conditions. The SO_2 removal in Run 935-2A averaged 73 percent at the average inlet SO_2 concentration of 2475 ppm, as compared to 76 percent SO_2 removal at 3200 ppm inlet SO_2 concentration in Run 718-2A with the Ceilcote type packing. The pressure drops across the packings including four bar grids averaged 9.1 and 7.2 inches H_2O for the Glitsch Grid and Ceilcote packing, respectively. The Glitsch Grid packing provided better overall particulate removal efficiency of 99.5 percent, compared to 98.9 percent with the Ceilcote type packing.

Under similar operating conditions listed in Table 21-1, a three-bed, four-grid TCA with 5 inches per bed static height of 1-5/8 inch diameter nitrile foam spheres (7 to 9 inches H_2O pressure drop) would give a predicted SO_2 removal of about 80 percent.

In summary, under similar operating conditions, Ceilcote egg-crate type packing gave better SO_2 removal, but lower pressure drop and lower particulate removal efficiency than the Glitsch Grid. Significantly less scale formation had been observed in the Ceilcote packing after 345 hours of operation (19 hours of pressure drop tests, 143 hours for Run 718-2A, and 183 hours for Run 719-2A) than Glitsch Grid type packing after 235 hours. The Glitsch Grid packing would not be expected to provide scale-free service in a limestone slurry scrubber.

Table 21-1

COMPARISON OF LIMESTONE TEST RESULTS
WITH GLITSCH GRID AND CEILCOTE TYPE PACKINGS

Major Test Condition	935-2A	718-2A
Gas rate, acfm @ 300°F	30,000	30,000
Slurry rate, gpm	1,200	1,200
Slurry solids concentration, wt %	15	15
Residence time, min.	12	12
Packing type	Glitsch Grid	Ceilcote
Packing height, inches	12	46
Number of packing layers	7	23
Run-Average Results		
Start-of-run date	12/2/80	11/24/77
On stream hours	128	143
Percent SO_2 removal(1)	73	76
Inlet SO_2 concentration, ppm	2,475	3,200
Average outlet mass loading, gr/dry scf	0.036	0.042
Percent mass removal efficiency	99.5	98.9
Scrubber inlet pH	5.75	5.75
Percent limestone utilization	81	75
Pressure drop, inches H_2O(2)	9.1	7.2
Scrubber inlet gypsum saturation, %	100	110
Mist eliminator restriction, %	<1	<1

(1) Under similar conditions, a three-bed, four-grid TCA with 5 inches/bed static height of 1-5/8 inch diameter nitrile foam spheres (7-9 inches H_2O pressure drop) would give a predicted SO_2 removal of about 80%.

(2) Pressure drop across the packing plus four bar grids.

21.3 LIMESTONE FACTORIAL TESTS

The Train 200 factorial tests (Runs TGG101 through TGG131) using about 1 ft (7 layers) of Glitsch Grid packing began on December 18, 1980, and terminated on January 7, 1981. Flue gas from Boiler No. 9 was used from December 18 through 29 because of a Boiler No. 10 tube failure. Boiler No. 10 flue gas was used from December 30 to January 7 after the boiler was restarted. Common operating conditions for this series were as follows:

Fly as loading: High (2 to 7 grains/dry scf)
Slurry solids concentration: 15 percent
Effluent hold tank (20 ft diameter) slurry level: 6 ft 2 in.
Solids dewatering equipment: Clarifier and filter

All tests were made without adipic acid and without forced oxidation. A summary of the results for these tests, including the major control variables, is presented in Table 21-2. Because of severe scaling of the packing, particularly at the scrubber inlet pH of 5.8, some of the runs had abnormally high pressure drop. These runs were repeated after the packing was cleaned on December 29 and 30.

Equation 21-1 for predicting SO_2 removal has been fitted to 25 Glitsch Grid runs (Runs TGG101 through TGG131)* for which the scrubber inlet pH was controlled at 5.0, 5.4. and 5.8 (see Table 21-2).

$$\text{Fraction } SO_2 \text{ Removal} = 1\text{-exp} \left[-7.9 \text{ X } 10^{-3}(L)^{.76}(G)^{-.54} \exp(0.91 \text{ pH})\right] \qquad (21\text{-}1)$$

where: L = slurry flow rate, gpm

G = gas flow rate, acfm @ 300°F

pH = scrubber inlet liquor pH

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* Runs TGG119, TGG122, TGG123, TGG126, TGG129 and TGG130 have not been included in the correlation because it was determined that during these runs there was excessive fouling of the Glitsch Grid packing.

Table 21-2

RESULTS OF LIMESTONE FACTORIAL TESTS WITH 1 FT GLITSCH GRID PACKING ON TRAIN 200

Run No	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		Scrubber Inlet Liquor pH		Scrubber Outlet Liq. pH	Ave. Cl^- conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Sulfite Oxid. (%)	L.S. Stoich	Replicate
				Total*	Packing**	Range	Ave.			Range	Ave.	Range	Ave.			
TGG101	20,000	1200	75	4.7	4.3	4.97-5.04	5.00	4.79	1420	2180-2360	2255	58.2-59.9	58.5	21.8	1.05	
TGG102	25,000	1200	60	6.8	6.4	5.05-5.10	5.05	4.58	710	2360-2600	2475	45.4-56.3	50.2	26.5	1.05	A
TGG103	30,000	1200	50	8.4	7.8	5.00	5.00	4.51	890	2500-2600	2575	43.6-45.4	44.2	32.7	1.05	
TGG104	25,000	1200	60	5.7	5.1	4.96-5.04	5.00	4.72	1430	2040-2320	2290	54.2-59.7	57.0	34.7	1.05	A
TGG105	20,000	900	56	4.3	3.9	5.10-5.18	5.15	4.60	920	2360-2520	2430	49.1-51.7	50.3	33.6	1.07	
TGG106	25,000	900	45	5.5	5.0	4.98-5.02	5.00	4.58	940	2360-2440	2420	37.1-40.1	39.2	25.3	1.08	B
TGG107	30,000	900	37	6.7	6.2	5.08-5.13	5.10	4.66	890	2320-2880	2660	38.1-45.7	41.0	25.3	1.08	
TGG108	25,000	900	45	4.5	4.0	4.94-5.02	5.00	4.84	1490	2080-2400	2270	46.8-51.8	49.1	26.2	1.05	B
TGG109	20,000	600	37	2.2	1.7	4.95-5.07	5.05	4.71	1600	2180-2240	2205	36.9-38.9	37.5	30.3	1.07	
TGG110	25,000	600	30	4.4	4.0	4.98-5.11	5.05	4.65	1030	2440-2520	2495	32.9-38.3	34.6	23.2	1.10	C
TGG111	30,000	600	25	4.7	4.0	4.95-4.97	4.95	4.68	1700	2120-2240	2180	31.4-33.2	32.8	25.0	1.05	
TGG112	25,000	600	30	3.2	2.7	5.05	5.05	4.60	1440	2220-2280	2250	37.1-38.7	37.8	35.3	1.08	C
TGG113	20,000	1200	75	5.5	5.1	5.37-5.45	5.40	4.87	975	2440-2560	2465	67.9-69.5	68.5	22.7	1.09	
TGG114	25,000	1200	60	7.0	6.5	5.28-5.46	5.40	5.02	1150	2360-2440	2400	56.7-60.4	58.5	21.1	1.11	
TGG115	30,000	1200	50	8.6	7.9	5.37-5.40	5.40	4.91	1180	2640-2720	2685	53.5-55.3	54.6	21.6	1.12	
TGG116	25,000	1200	60	5.6	5.2	5.29-5.43	5.40	4.95	1385	2160-2320	2220	65.9-71.2	69.3	25.4	1.07	D
TGG117	20,000	900	56	4.5	4.1	5.39-5.42	5.40	-	-	2600-2720	2660	54.6-56.7	56.5	-	1.04	
TGG118	25,000	900	45	6.1	5.8	5.31-5.38	5.35	-	-	2320-2720	2575	48.7-53.1	50.4	-	1.13	E
TGG119	30,000	900	37	8.1	7.5	5.34-5.42	5.40	5.00	1400	2680-2880	2790	44.5-47.8	46.5	20.0	1.15	
TGG120	25,000	900	45	4.6	4.2	5.45	5.45	5.18	1315	2200-2400	2295	58.3-63.0	61.5	26.3	1.09	E
TGG121	20,000	600	37	1.7	1.3	5.45	5.45	4.99	1440	2160-2200	2170	46.0-49.6	48.2	28.7	1.07	
TGG122	25,000	600	30	5.6	5.1	5.26-5.41	5.35	4.84	1385	2360-2680	2565	37.8-40.7	39.5	19.9	1.11	F
TGG123	30,000	600	25	7.8	7.3	5.33-5.44	5.40	4.94	1475	2560-2640	2600	37.8-41.6	40.5	13.5	1.17	
TGG124	25,000	600	30	3.3	2.8	5.41-5.45	5.45	4.99	1545	2400-2460	2430	45.9-47.7	46.5	22.4	1.10	F
TGG126	25,000	1200	60	10.8	10.3	5.68-5.76	5.75	5.30	1530	2520-2680	2630	70.5-73.1	72.0	21.9	1.18	G
TGG126(R)	25,000	1200	60	6.8	6.2	5.60-5.62	5.60	5.14	1600	2280-2500	2385	70.5-73.3	71.5	17.3	1.22	G
TGG129	20,000	900	56	8.5	8.2	5.73-5.82	5.80	5.35	1420	2320-2460	2410	70.9-71.8	71.5	21.7	1.27	H
TGG129(R)	20,000	900	56	4.2	3.9	5.72-5.75	5.75	5.30	1560	2360-2440	2385	72.9-76.0	75.3	26.0	1.26	H
TGG130	25,000	900	45	17.5	17.2	5.78-5.83	5.80	5.40	1510	2080-2160	2120	72.8-77.4	74.9	29.1	1.26	I
TGG130(R)	25,000	900	45	5.6	4.9	5.82-5.85	5.85	5.41	1560	2040-2440	2290	70.9-78.8	72.8	13.6	1.48	I
TGG131	30,000	900	37	7.0	6.2	5.72-5.76	5.75	5.23	1510	2440-2520	2465	66.6	66.6	14.7	1.28	

* ΔP Between taps in front of presaturator and after mist eliminator (M.E.)

**ΔP Across 1 ft. Glitsch Grid packing and 4 bar grids

The ranges of operating variables covered by the 25 correlated runs are:

pH = 4.95 to 5.85
Gas flow rate = 20,000 to 30,000 acfm @ 300°F
= 8.4 to 12.5 ft/sec @ 125°F (saturated)
Slurry flow rate = 600 to 1200 gpm
= 18.8 to 37.5 gpm/ft^2
Inlet SO_2 concentration = 2170 to 2685 ppm
Sulfite oxidation = 13.6 to 35.3 percent (natural oxidation)

Figure 21-2 shows measured values of SO_2 removal plotted against values predicted by Equation 21-1. Equation 21-1 explains 92.2 percent of the variation in the data for SO_2 removal with a standard error of estimate of 3.5 percent SO_2 removal.

Figures 21-3 through 21-5 illustrate the effects of gas and slurry flow rates on SO_2 removal at scrubber inlet pH of 5.0, 5.4, and 5.8, respectively. The lines on the figures represent the predictions of Equation 21-1 with actual data points also shown.

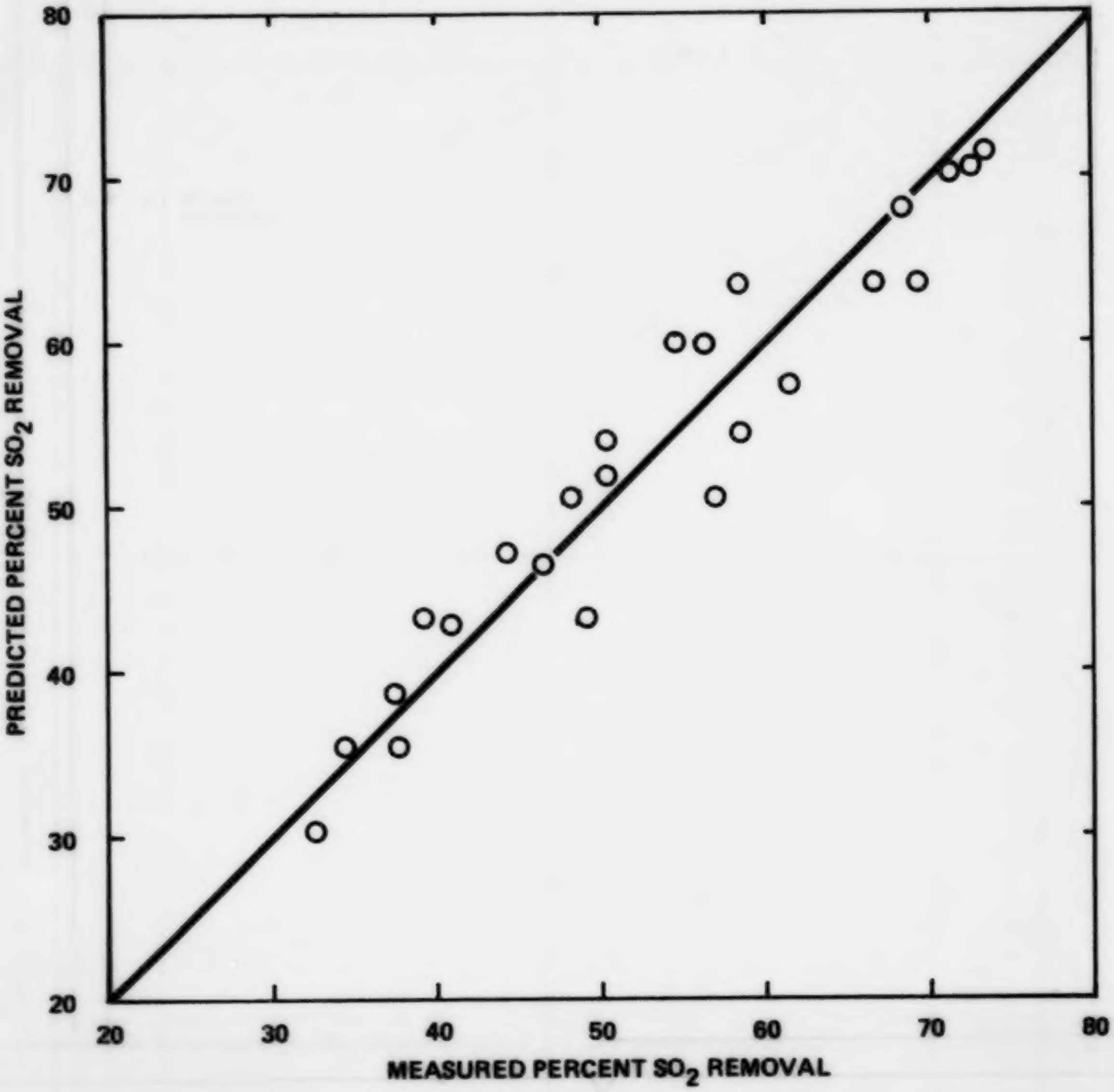


Figure 21-2

Measured vs. Predicted Percent SO_2 Removal
In The Glitsch Grid Packed Scrubber

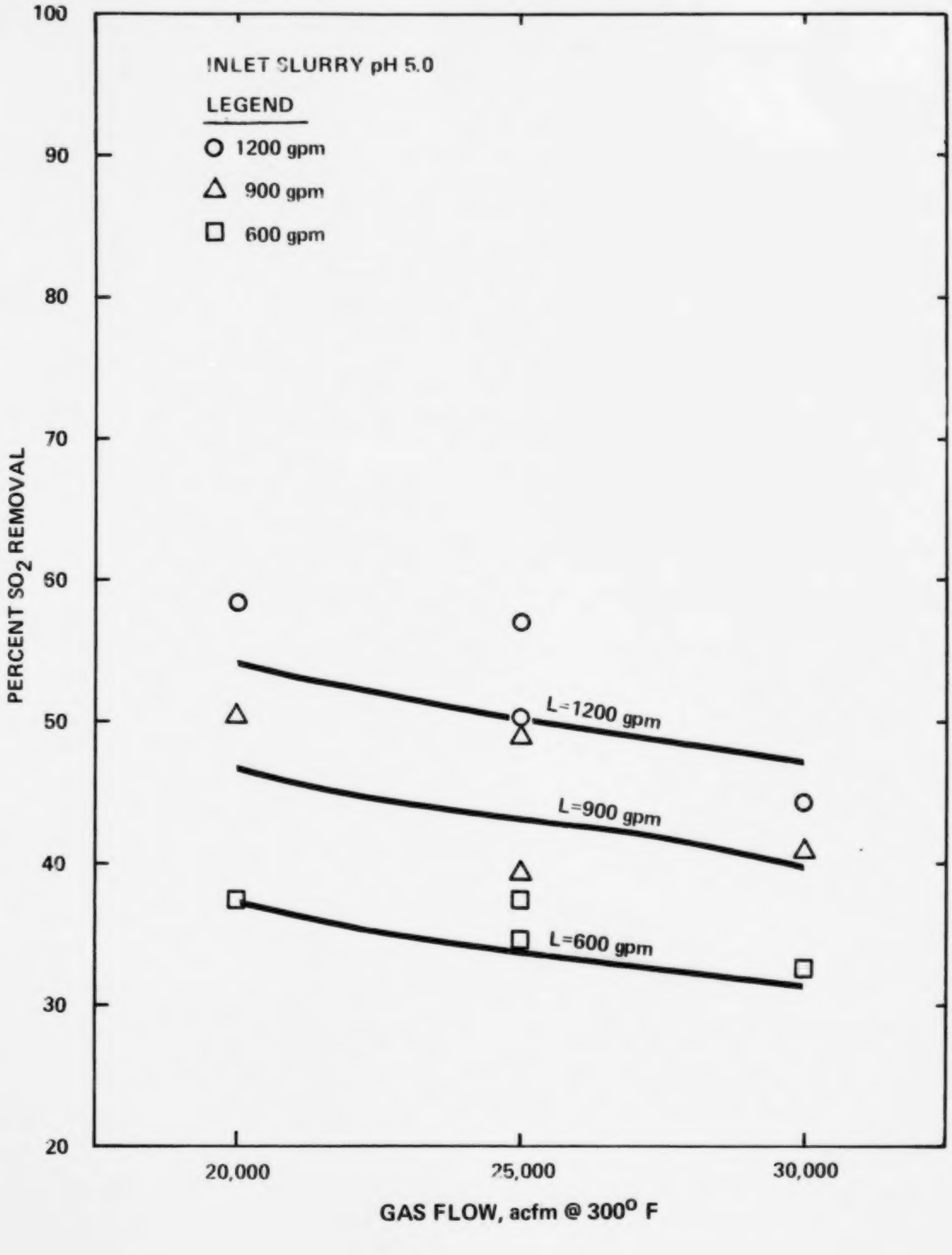


Figure 21-3

Glitsch Grid Scrubber SO_2 Removal vs. Gas And Slurry Flow Rates At 5.0 Scrubber Inlet pH

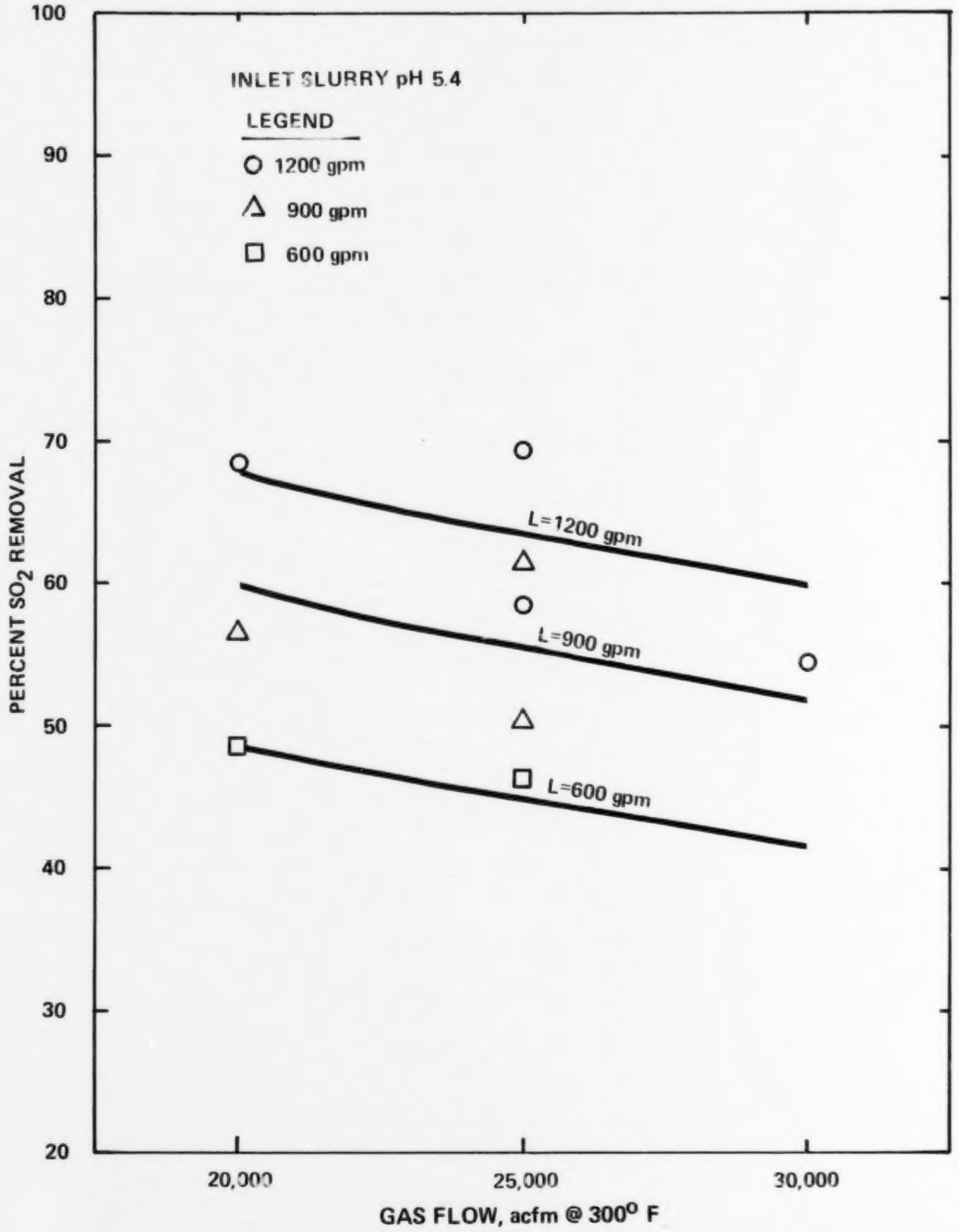


Figure 21-4

Glitch Grid Scrubber SO_2 Removal vs. Gas And Slurry Flow Rates At 5.4 Scrubber Inlet pH

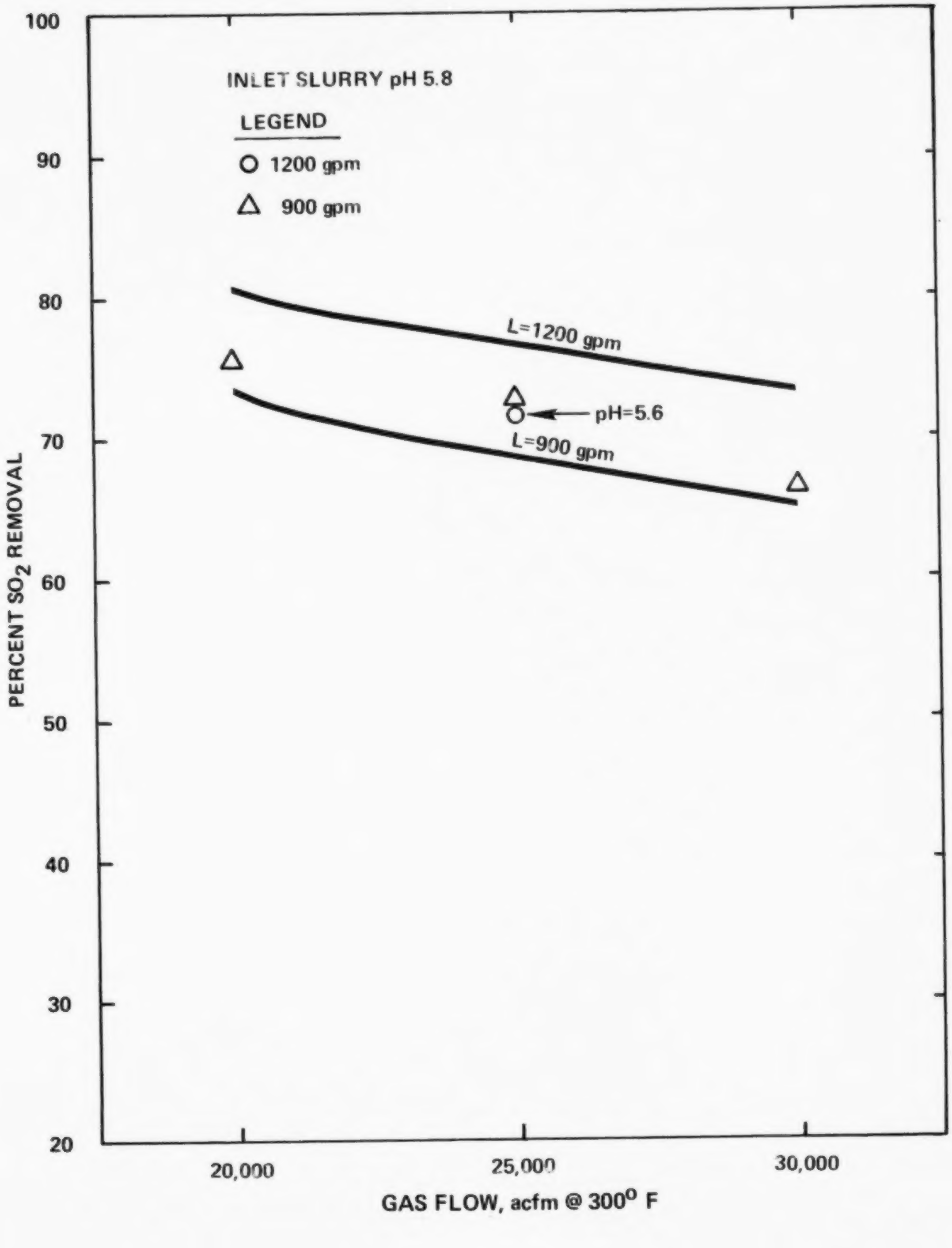


Figure 21-5

Glitsch Grid Scrubber SO_2 Removal vs. Gas And Slurry Flow Rates at 5.8 Scrubber Inlet pH

Section 22

FACTORIAL TEST RESULTS AND MATHEMATICAL MODELING

Full or partial factorial tests have been conducted in order to characterize the SO_2 removal performance of the scrubbers as a function of operating parameters, such as gas velocity, slurry flow rate (liquid-to-gas ratio), slurry pH, additive concentration, etc. These tests usually lasted 12 hours or longer, including at least 5 to 7 hours of steady-state operation.

Because of the nature of the testing, the ranges of operating conditions selected were sometimes extreme by necessity and were not always conducive to reliable system operation. On the other hand, tests without scaling or plugging problems do not necessarily infer long-term reliability, because of their short duration.

This section presents the results of the factorial tests and, wherever possible, the correlations of data using a semi-theoretical model.

22.1 DEVELOPMENT OF THE MODEL

The correlations of Shawnee data for SO_2 removal follow the form of a semi-theoretical mathematical model that is compatible with boundary constraints on SO_2 removal and the operating variables (e.g., SO_2 removal as predicted by the model varies between zero and 100 percent, with zero removal at zero slurry flow rate). The correlations permit reasonable extrapolations beyond the range of fitted data. For the TCA, the possibility of flooding due to excessive pressure drop (see Section 28) should be considered when extrapolating beyond the ranges of gas and slurry flow rates investigated.

For absorption of SO_2 from the gas phase into the liquid phase, the following differential equation applies (Reference 22):

$$-v\ d(SO_2) = K_G a\ [SO_2 - (SO_2)_e]\ dz = [SO_2 - (SO_2)_e]dz/\left[\frac{1}{k_G a} + \frac{H}{k_L^o a \phi}\right] \qquad (22\text{-}1)$$

where:

K_G = overall gas mass transfer coefficient, based on both liquid-side and gas-side resistances to mass transfer, ft/sec

k_G = gas-side mass transfer coefficient, ft/sec

k_L^o = liquid-side mass transfer coefficient for physical absorption, ft/sec

a = gas-liquid interfacial area per scrubber volume, ft^2/ft^3

ϕ = average chemical reaction enhancement factor for mass transfer in the liquid film, dimensionless

v = scrubber gas velocity, ft/sec

z = vertical distance in the scrubber, ft

SO_2 = mole fraction of SO_2 in the gas phase at a given value of z

$(SO_2)_e$ = mole fraction of SO_2 in the gas phase that would be in equilibrium with the liquid phase

H = Henry's Law constant for SO_2, mole fraction in gas/mole fraction in liquor

Analysis of typical Shawnee limestone/lime wet scrubbing liquors, by use of the Bechtel modified equilibrium computer program (see Appendix K), has shown that the equilibrium SO_2 is much less than the actual SO_2 [i.e., $(SO_2)_e << SO_2$]. Also a comparison of Shawnee limestone/lime scrubbing data with earlier Shawnee data for gas-side controlled soda ash scrubbing (Reference 1) has shown that the liquid side resistance is dominant, i.e., $k_L^o\phi/H << k_G$ for limestone/lime scrubbing. Under these conditions, Equation 22-1 can be simplified to:

$$-v\ d(SO_2) = (k_L^o a\phi/H)\ SO_2\ dz \qquad (22\text{-}2)$$

Assuming that the ratio ($k_L^o a \phi /H$) is constant, integration of Equation 22-2 across the entire height of the scrubber yields:

$$\text{Fraction Removal } SO_2 = 1 - \exp [-\phi k_L^o az/Hv] \qquad (22\text{-}3)$$

In Equation 22-3, the physical absorption group, $k_L^o az/H$, can be expressed in a form that fits boundary constraints on SO_2 removal, gas and slurry flow rates, and total static height of spheres (for TCA only):

$$k_L^o az/Hv = \alpha_1 L^{\alpha_2} (1/v)^{\alpha_3} \exp (\alpha_4 h_s) \qquad (22\text{-}4)$$

where:

L = slurry flow rate per unit scrubber cross-sectional area, gpm/ft^2

h_s = total static height of spheres in the TCA, inches (zero for the spray tower)

α's = positive constant coefficients to be fitted to limestone/lime wet-scrubbing data

Equation 22-4 conforms to the expectation that ($k_L^o a$) increases with slurry flow rate (Reference 22) and that ($k_L^o az$) in the TCA increases with static height of spheres.

The enhancement factor ϕ in Equation 22-3 represents the chemical reactivity of the scrubber liquor with absorbed SO_2 gas. This chemical reactivity should increase with increased scrubber liquor pH, increased additive (adipic acid) concentration, and decreased inlet gas SO_2 concentration. An empirical relationship for ϕ , expressed in terms of these variables and compatible with boundary constraints on SO_2 removal, is:

$$\phi = \exp[\alpha_5 pH_i + \alpha_6 A - \alpha_7 (SO_2)_i] \qquad (22\text{-}5)$$

where:

pH_i = scrubber inlet liquor pH

A = additive (adipic acid) concentration, ppm

$(SO_2)_i$ = scrubber inlet gas SO_2 concentration, ppm

α's = positive constant coefficients fitted to the data

Equation 22-5 predicts that SO_2 removal efficiency decreases with increasing $(SO_2)_i$. For the mass transfer conditions in limestone/lime scrubbing, i.e., negligible $(SO_2)_e$ and negligible gas phase resistance, $SO_2(aq)$ at the gas-liquid interface increases in direct proportion to the SO_2 gas concentration. This increase in $SO_2(aq)$ lowers the pH at the interface, reducing liquor reactivity and the fraction of SO_2 gas absorbed.

The semi-theoretical form of the model for fraction SO_2 removal is obtained by combining Equations 22-3 through 22-5:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left\{- \alpha_1 L^{\alpha_2}(1/v)^{\alpha_3} \cdot \exp\left[\alpha_4 h_s + \alpha_5 pH_i + \alpha_6 A - \alpha_7 (SO_2)_i\right]\right\} \qquad (22\text{-}6)$$

Equation 22-6 has been correlated to Shawnee spray tower and TCA limestone/lime data. The operating variables having the greatest statistical significance in fitting the data were slurry flow rate in the TCA, liquid-to-gas ratio (proportional to L/v) in the spray tower, scrubber inlet liquor pH, adipic acid concentration, and total static height of spheres in the TCA.

During factorial tests conducted in the reporting period, the variations in $(SO_2)_i$ were not sufficiently large (typically 2000 to 3000 ppm) to have a significant influence on the fitted correlations. Therefore, the term $(SO_2)_i$ in Equation 22-6 was excluded.

22.2 VENTURI ONLY WITH LIME/ADIPIC ACID WITHOUT FORCED-OXIDATION

A total of 14 lime/adipic acid factorial tests (Runs VAA101 through VAA114) were conducted in April, May and October 1979 using the venturi scrubber only (spray tower slurry flow turned off). All tests were made without forced oxidation. The flue gas flow rate (liquid-to-gas ratio) and adipic acid concentration were varied to observe their effect on the SO_2 removal. Operating conditions held constant during these tests were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Venturi inlet pH:	6.0
Venturi pressure drop:	9 inches H_2O
Venturi slurry flow rate:	600 gpm
Slurry solids concentration:	8 percent
Hold tank residence time:	24 minutes

The test results are listed in Table 22-1.

The effect of adipic acid concentration on SO_2 removal has been correlated for 12 of the 14 runs (Runs VAA112 and VAA114 were adipic acid depletion tests) by the folowing equation:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left[-0.48 \exp\left(3.3 \times 10^{-4} A\right)\right] \qquad (22\text{-}7)$$

where: A is the adipic acid concentration in ppm.

Adipic acid concentrations were varied between 800 and 3200 ppm. Gas flow rate, which varied from 20,000 to 35,000 acfm (@ 300°F), had no significant effect on the SO_2 removal.

Equation 22-7 explains 89 percent of the variation in the data for SO_2 removal, with a standard error of estimate of 3.3 percent SO_2 removal.

Figure 22-1 shows SO_2 removal as a function of adipic acid concentration for

Table 22-1

RESULTS OF LIME/ADIPIC ACID FACTORIAL TESTS USING THE VENTURI ONLY

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Press. Drop (in H_2O)	Venturi Inlet Liquor pH		Venturi Outlet Liq. pH	Ave. $AD^=$ Conc (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Replicate
					Range	Ave.				Range	Ave.	Range	Ave.	
VAA101	20,000	587	37	8.8	5.99-6.14	6.06	4.60	1700	2925	2700-2800	2762	58-60	59.4	
VAA102	32,500	587	22	8.9	5.98-6.15	6.07	4.60	1545	2441	2360-2760	2585	54-59	56.2	G
VAA103	27,500	589	26	8.8	6.13-6.24	6.19	4.90	1637	2352	2700-2880	2799	57-61	59.4	
VAA104	33,000	591	22	9.0	6.03-6.23	6.13	4.50	1602	2396	2480-2680	2596	54-57	55.8	G
VAA105	20,000	587	37	9.1	5.63-6.16	5.88	4.90	2412	2086	2840-3040	2943	62-65	63.7	
VAA106	32,500	590	22	9.1	5.62-6.10	5.87	4.60	2153	2529	2480-2640	2562	54-58	55.8	
VAA107	27,500	583	26	9.0	5.46-6.15	5.87	4.60	2076	2529	2720-3000	2858	55-62	58.4	
VAA108	20,000	597	37	9.0	6.00-6.48	6.20	5.40	2821	2860	1680-1800	1742	72-78	75.5	H
VAA109	35,000	590	21	9.0	5.91-6.34	6.09	-	3079	2308	1720-2000	1863	69-75	71.2	
VAA110	27,500	597	26	8.8	5.74-6.65	6.06	5.30	3172	3191	1600-1800	1666	73-77	74.8	
VAA111	20,000	598	37	9.0	5.87-6.15	5.99	5.40	3042	3077	1680-1800	1771	73-74	73.8	H
VAA112(1)	20,000	593	37	9.0	5.47-6.50	5.97	5.24	4090 → 750	3132	1760-2480	2220	74 → 46	-	
VAA113	20,000	590	37	8.9	5.82-6.43	6.04	5.17	848	2130	2120-2280	2224	45-49	46.8	
VAA114(1)	20,000	591	37	8.9	5.35-6.60	6.02	5.80	770 → 140(2)	1238	1880-2480	2166	47 → 27	-	

(1) Adipic acid depletion tests.
(2) Open-loop operation.

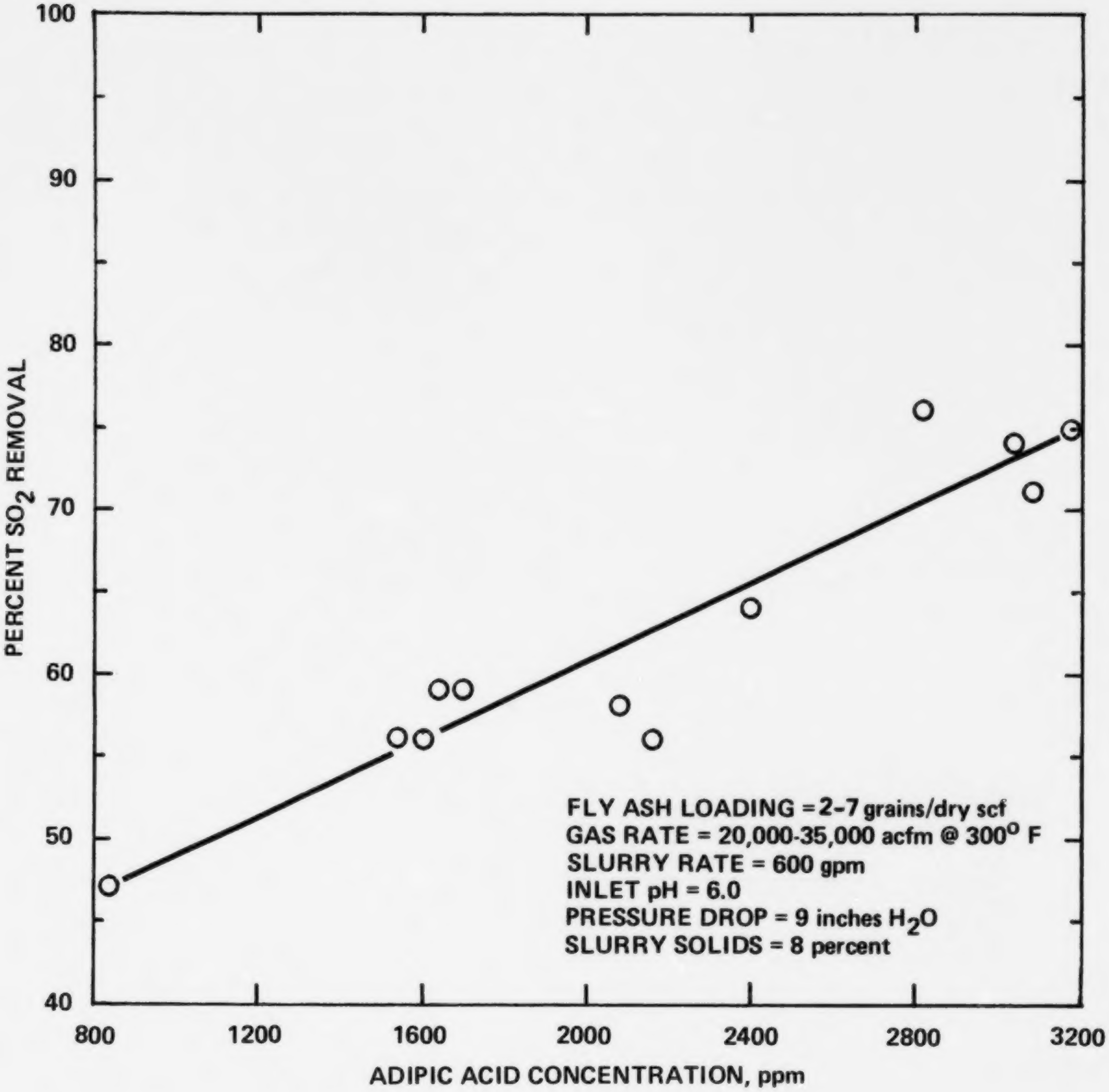


Figure 22-1

Effect Of Adipic Acid Concentration On SO_2 Removal
In The Venturi With Lime Scrubbing

the venturi with lime scrubbing. The curve in Figure 22-1 is predicted by Equation 22-7; the actual data points (run-averages) are also shown. The SO_2 removal is linear with adipic acid concentration for the operating range tested, increasing from 49 percent at 1000 ppm adipic acid to 61 percent at 2000 ppm, and to 73 percent at 3000 ppm.

Figure 22-2 is a plot of venturi hourly SO_2 removal data as a function of adipic acid concentration during the adipic acid depletion tests (Runs VAA112 and VAA114). A comparison of Figures 22-1 and 22-2 shows the SO_2 removals to be in good agreement. Extrapolation of Figure 22-2 to zero adipic acid concentration gives 25 to 30 percent SO_2 removal, which is typical for the Shawnee venturi when to adipic acid is used.

22.3 VENTURI/SPRAY TOWER WITH LIMESTONE/ADIPIC ACID AND TWO-SCRUBBER-LOOP OPERATION

In the period from July 6 through October 3, 1979, a series of 54 partial factorial tests was conducted on the venturi/spray tower system with limestone/adipic acid slurry. These tests were made to investigate the effects on SO_2 removal of the following variables:

- Adipic acid concentration in liquor
- Gas flow rate and venturi/spray tower slurry flow rates (liquid-to-gas ratios)

The flow configuration of the two-scrubber-loop system used in these tests is shown in Figure 4-1. Tests were conducted both with and without forced oxidation. The arrangement of the oxidation tank is shown in Figure 4-2.

During the majority of tests, inlet flue gas SO_2 concentrations ranged from

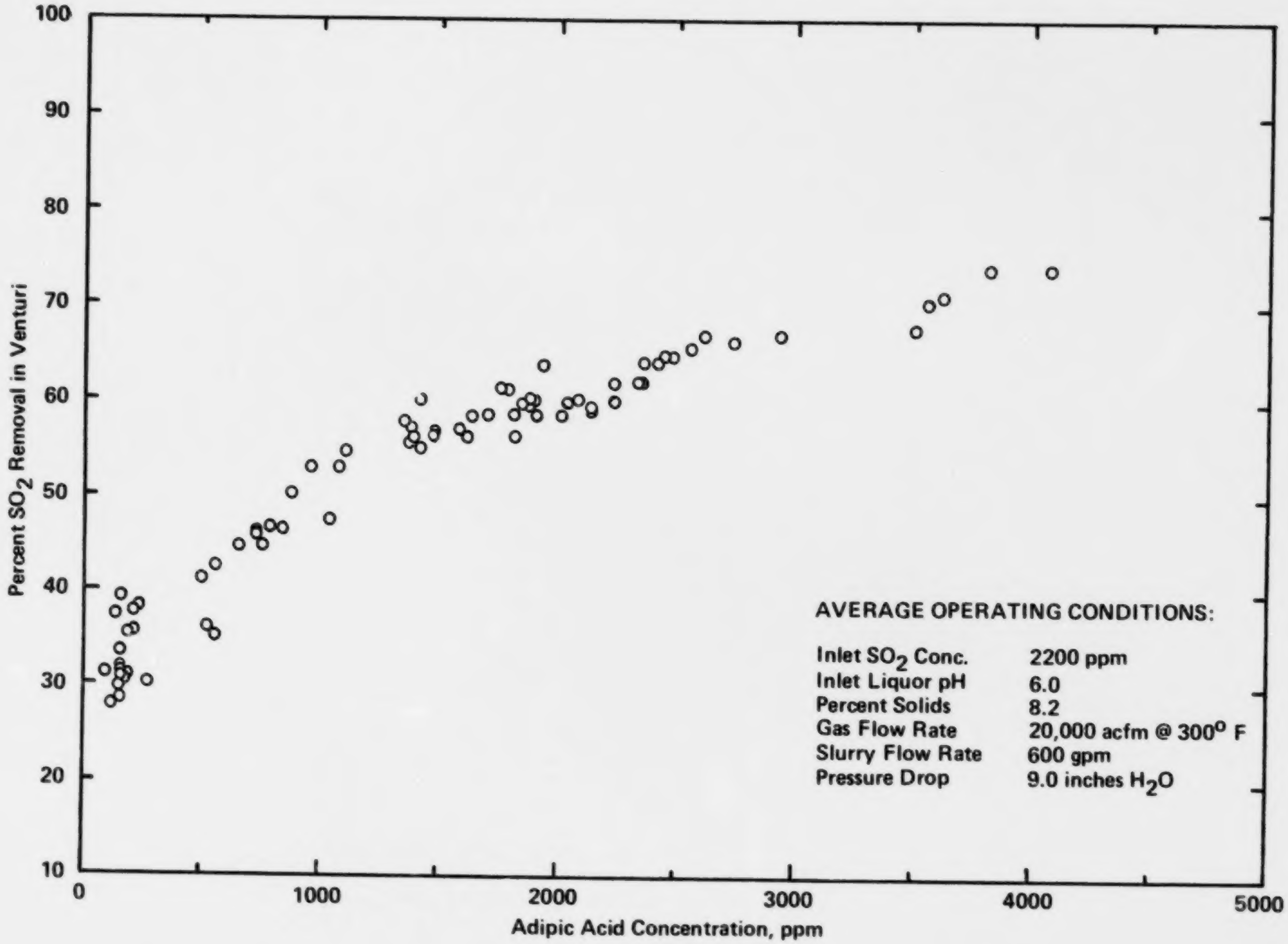


Figure 22-2. Percent SO_2 Removal vs. Adipic Acid Concentration During Adipic Acid Depletion Lime Runs VAA112 and VAA114 on the Venturi

1800 to 2800 ppm (high sulfur coal). In 7 runs, however, low sulfur coal was burned in Boiler No. 10 and the inlet SO_2 concentrations dropped to a low range of 800 to 1800 ppm. Test results for runs with high and low sulfur coals are listed separately in Tables 22-2 and 22-3, respectively.

The 54 runs were divided into three groups of testing (see footnotes of Tables 22-2 and 22-3):

(1) Venturi and spray tower two-scrubber-loop tests without forced oxidation and with open-liquor-loop operation (no clarified liquor or filtrate was returned to the system).

(2) Closed loop, spray tower only operation without forced oxidation (two-scrubber-loop with the venturi plug wide open at a minimum slurry flow of 125 gpm).

(3) Closed loop, venturi and spray tower two-scrubber-loop tests with forced oxidation in the venturi loop.

Test group (1) was made to observe the effect of fresh adipic acid on SO_2 removal as compared to Test Group (3) in which the recycled (degraded) adipic acid from the dewatering system made up most of the adipic acid in the scrubber loops. Tests group (2) was made to investigate the SO_2 removal efficiency with the spray tower alone.

The operating conditions common to all the factorial tests were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Spray tower hold tank level (20-ft diameter):	10 ft
Oxidation tank level (8-ft diameter):	18 ft
Desupersaturation tank level (10-ft diameter):	4.8 ft
Venturi slurry flow rate:	600 gpm for test groups (1) & (3), 125 gpm for test group (2)
Venturi inlet pH:	Greater than 4.5 for test groups (1) & (3)
Spray tower limestone stoichiometry:	1.7 for test groups (1) & (3), 1.2 for test group (2)
Air flow rate to oxidizer:	220 scfm for test group (3) only
Venturi slurry solids conc.:	15 percent for test groups (1) & (3), uncontrolled for test group (2)
Spray tower slurry solids conc.:	6 percent for test groups (1) & (3), 15 percent for test group (2)
Venturi pressure drop:	9 in. H_2O for test groups (1) & (3), wide open plug for test group (2)

Table 22-2

RESULTS OF LIMESTONE/ADIPIC ACID FACTORIAL TESTS ON THE TWO-SCRUBBER-LOOP VENTURI/SPRAY TOWER SYSTEM USING HIGH SULFUR COAL

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)		ST Gas Velocity (ft/sec)	ST L/G (gal/mcf)	Pressure Drop (inch H_2O)		Inlet Liquor pH		ST Outlet Liquor pH	Ave. ST AD* Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Replicate	Notes
		Venturi	ST(1)			Venturi	Total	Venturi	ST				Range	Ave.	Range	Ave.		
VAA-001	35,000	591	1263	9.4	45	9.0	14.3	5.84	6.27	-	309	222	2320-2520	2410	91-93	92.0		(2)
VAA-002	35,000	586	1606	9.4	57	9.0	14.8	5.73	6.37	-	343	178	2280-2440	2327	94-97	95.5		(2)
VAA-003	35,000	586	1596	9.4	57	8.5	14.1	5.71	6.33	6.3	595	178	2240-2680	2482	96-98	97.5		(2)
VAA-004	35,000	586	1221	9.4	44	8.9	14.1	5.89	6.37	6.2	588	228	2400-2560	2504	95-96	95.3		(2)
VAA-005	27,500	122	1203	7.4	55	2.7	5.8	5.78	5.86	5.5	693	1464	2240-2540	2357	84-90	86.4	A	(3)
VAA-006	35,000	125	1204	9.4	43	4.2	9.1	5.55	5.97	5.8	597	888	2520-2640	2557	79-82	80.4	G	(3)
VAA-007	27,500	125	1231	7.4	56	3.1	6.1	5.81	6.01	5.8	608	977	2320-2600	2451	87-91	89.1	A	(3)
VAA-008	20,000	123	1206	5.4	75	1.5	3.2	5.79	5.90	5.7	601	1598	2000-2120	2062	94-96	94.7	H	(3)
VAA-009	20,000	122	1590	5.4	99	2.1	2.9	5.90	5.91	5.7	646	1420	2000-2120	2097	98	98.0		(3)
VAA-010	35,000	125	799	9.4	29	4.6	9.6	5.33	5.84	5.6	594	1420	1820-2320	2216	72-77	74.3		(3)
VAA-311	35,000	593	788	9.4	28	9.0	14.8	5.03	5.92	5.7	620	1627	2360-2480	2428	77-80	78.7		(4)
VAA-312	20,000	600	1550	5.4	97	8.7	10.6	5.35	5.91	5.9	693	1997	2120-2320	2186	97-98	97.6		(4)
VAA-313	27,500	595	1188	7.4	54	9.4	13.1	5.09	5.90	5.6	658	2325	2200-2280	2239	92-94	93.5	B	(4)
VAA-314	35,000	598	1190	9.4	43	9.0	15.1	5.23	5.82	5.6	653	2574	2220-2300	2263	90-91	90.6		(4)
VAA-315	20,000	594	1191	5.4	74	9.0	10.6	5.42	5.81	5.6	723	2529	2200-2280	2238	96-97	96.5		(4)
VAA-316	27,500	590	1188	7.4	54	8.9	12.4	4.63	5.92	5.6	665	2663	2120-2320	2207	91-93	92.3	B	(4)
VAA-017	35,000	591	1191	9.4	43	9.0	14.6	4.94	6.01	5.8	1012	1213	2400-2480	2429	89-92	91.5		(2)
VAA-018	35,000	596	1596	9.4	57	9.0	15.3	4.66	6.08	5.7	1037	337	2320-2480	2389	94-97	95.6		(2)
VAA-019	35,000	596	1598	9.4	57	8.9	14.5	5.34	6.17	6.1	1438	182	2000-2320	2167	98-99	98.2		(2)
VAA-020	35,000	598	1203	9.4	43	9.2	14.9	4.66	6.09	5.9	1177	275	2080-2240	2170	94-98	94.6		(2)
VAA-021	27,500	123	1192	7.4	54	2.2	6.3	4.76	5.54	5.3	1247	2535	2400-2520	2484	88-91	89.0	C	(3)
VAA-022	20,000	120	1198	5.4	74	1.5	3.0	5.08	5.61	5.4	1354	2840	2200-2300	2269	94-95	94.7		(3)
VAA-023	35,000	122	1196	9.4	43	3.5	8.8	5.06	5.77	5.5	1294	3195	1800-2160	1973	89-93	91.0		(3)
VAA-024	27,500	120	1198	7.4	54	2.3	5.2	4.93	5.56	-	1270	3816	2240-2360	2310	89-91	89.9	C	(3)
VAA-025	35,000	122	794	9.4	28	3.0	8.7	4.75	5.51	5.3	1288	2814	2400-2680	2587	73-76	73.9		(3)
VAA-026	20,000	122	1599	5.4	99	1.4	3.7	5.21	5.67	5.5	1430	2769	1880-2000	1942	96-98	96.7		(3)
VAA-027	20,000	599	1603	5.4	100	8.9	10.5	5.19	6.04	5.8	1363	612	2040-2120	2057	98-99	98.9		(4)
VAA-028	35,000	599	795	9.4	28	9.3	15.1	4.80	5.38	5.0	1459	1917	2260-2520	2426	86-90	86.9		(4)
VAA-029	27,500	598	1197	7.4	54	9.0	12.3	4.83	5.86	5.6	1211	941	2240-2480	2392	96-97	96.4	D	(4)
VAA-030	20,000	597	1205	5.4	75	9.0	10.4	4.99	5.98	5.7	1396	905	2200-2440	2277	98-99	98.4		(4)
VAA-031	35,000	594	1175	9.4	43	9.0	14.7	4.88	5.65	5.4	1477	1702	2360-2540	2951	94-95	94.4		(4)
VAA-032	27,500	598	1192	7.4	54	9.0	12.5	4.81	5.70	5.5	1209	1775	2320-2520	2411	96-97	96.8	D	(4)
VAA-035	35,000	588	795	9.4	28	8.9	14.9	4.59	5.59	5.4	2054	3343	2240-2400	2358	88-92	89.6		(2)
VAA-036	35,000	125	796	9.4	28	4.0	9.1	4.77	5.55	5.3	2238	4371	2360-2500	2455	82-84	83.3		(3)
VAA-037	20,000	124	1596	5.4	100	1.4	3.3	5.00	5.58	5.4	2139	4438	2440-2640	2547	98	98.0		(3)
VAA-038	35,000	118	1200	9.4	43	3.4	8.6	4.62	5.75	5.4	1802	3787	2200-2360	2259	88-90	88.2	E	(3)
VAA-039	27,500	125	1197	7.4	54	2.3	5.4	4.89	5.58	5.4	2081	4438	2400-2480	2453	90-92	90.9		(3)
VAA-040	20,000	125	1195	5.4	75	1.5	3.0	5.05	5.64	5.3	1830	4526	2320-2520	2438	95-96	95.9		(3)
VAA-041	35,000	126	1194	9.4	43	3.7	9.1	4.87	5.65	5.3	1773	4171	2680-2800	2697	85-86	85.1	E	(3)
VAA-042	35,000	126	400	9.4	14	3.7	8.8	4.79	5.62	5.4	1973	3861	2400-2560	2456	59-61	60.5		(3)
VAA-043	35,000	589	797	9.4	28	9.0	15.1	4.71	5.24	5.1	2059	3994	2200-2400	2317	89-92	90.2	F	(4)
VAA-044	35,000	587	1209	9.4	43	9.0	15.1	4.96	5.65	5.5	1853	3595	2080-2200	2118	95-96	95.8		(4)
VAA-045	27,500	589	1205	7.4	55	8.9	13.1	5.07	5.75	5.3	2124	4083	2200-2520	2321	97-98	97.4		(4)
VAA-046	20,000	590	1207	5.4	75	8.8	10.7	4.89	5.33	5.1	1959	4319	2240-2280	2265	97-98	97.4		(4)
VAA-048	35,000	586	794	9.4	28	9.0	15.0	4.74	5.21	5.0	2124	5029	2320-2440	2388	86-88	87.0	F	(4)
VAA-306	35,000	124	1190	9.4	43	5.0	11.3	4.94	5.75	5.3	597	2201	2120-2440	2316	77-81	80.1	G	(3)
VAA-308	20,000	125	1190	5.4	75	1.8	3.6	5.16	5.86	5.7	591	1864	1800-2240	2011	90-93	91.7	H	(3)

Notes:

(1) Spray tower slurry flow rates are in 400 gpm increments (400, 800, 1200, and 1600 gpm). For 1600 gpm full flow rate, all 4 headers are used at 400 gpm/header. Headers are turned off starting from the bottom header for runs using less than 1600 gpm.

(2) Venturi and spray tower two-scrubber-loop tests without forced oxidation and with open-liquor-loop operation.

(3) Spray tower only operation (venturi plug wide open with 140 gpm minimum slurry flow) without forced oxidation.

(4) Venturi and spray tower two-scrubber-loop tests with forced oxidation.

Table 22-3

RESULTS OF LIMESTONE/ADIPIC ACID FACTORIAL TESTS ON THE TWO-SCRUBBER-LOOP VENTURI/SPRAY TOWER SYSTEM USING LOW SULFUR COAL

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)		ST Gas Velocity (ft/sec)	ST L/G (gal/mcf)	Pressure Drop (inch H_2O)		Inlet Liquor pH		ST Outlet Liquor pH	Ave. ST $AD^=$ Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration, (ppm)		Percent SO_2 Removal		Replicate	Notes
		Venturi	ST(1)			Venturi	Total	Venturi	ST				Range	Ave.	Range	Ave.		
VAA-305	27,500	116	1190	7.4	55	3.6	8.7	4.99	5.54	5.2	629	2130	1480-1600	1520	73-86	82.0		(2)
VAA-011	35,000	589	784	9.4	28	9.0	15.4	5.09	6.15	6.0	637	1154	800-1680	1347	89-98	94.2		(3)
VAA-012	20,000	585	1595	5.4	100	9.0	10.9	5.08	5.84	5.7	687	1625	1080-1400	1304	96-98	96.9		(3)
VAA-013	27,500	592	1191	7.4	55	9.0	12.9	5.14	6.28	5.9	665	1310	1320-1600	1458	95-97	95.9	B	(3)
VAA-014	35,000	584	1193	9.4	43	9.1	15.4	4.80	6.02	5.8	643	1287	1600-1780	1698	92-94	93.2		(3)
VAA-015	20,000	587	1198	5.4	75	9.0	11.4	5.29	5.91	5.6	704	1674	1280-1600	1420	97-98	97.4		(3)
VAA-016	27,500	586	1196	7.4	55	8.8	12.7	5.15	6.18	5.9	562	1154	1360-1680	1502	96-98	96.8	B	(3)

Notes:

(1) Spray tower slurry flow rates are in 400 gpm increments (400, 800, 1200, and 1600 gpm). For 1600 gpm full flow rate, all 4 headers are used at 400 gpm/header. Headers are turned off starting from the bottom header for runs using less than 1600 gpm.

(2) Spray tower only operation (venturi plug wide open with 140 gpm minimum slurry flow) without forced oxidation.

(3) Venturi and spray tower two-scrubber-loop tests with forced oxidation.

For a given controlled level of adipic acid concentration in the spray tower liquor, the corresponding adipic acid concentrations in the venturi liquor was normally about 50 percent higher. Flue gas humidification (evaporation of water) in the venturi resulted in higher dissolved species concentration in the venturi loop.

With controlled limestone stoichiometry, the spray tower inlet slurry pH was high, ranging from 5.21 to 6.37.

The spray tower slurry flow rates were in 400 gpm increments (400, 800, 1200, and 1600 gpm). For the maximum flow rate of 1600 gpm, all four spray headers (spaced 4 ft apart) were used with 400 gpm/header. Headers were turned off starting from the bottom header for runs using less than 1600 gpm. Each header had seven Bete No. ST48FCN nozzles. The top three headers sprayed the slurry downward while the bottom header sprayed upward.

22.3.1 Testing with Spray Tower Only--Test Group (2)

In the original equipment set-up in Train 100 as shown in Figure 4-1, the flue gas could not be by-passed around the venturi scrubber for testing with the spray tower alone. In this series of tests, a compromise was made by operating the venturi with a wide-open plug and with the minimum controllable slurry flow rate of 125 gpm for flue gas cooling to protect the neoprene lining of the spray tower. This mode of operation minimizes the effect of the venturi on SO_2 removal and allows the evaluation of the spray tower performance.

Unfortunately, with adipic acid-enhanced scrubbing, a significant amount of SO_2 was removed in the venturi even though only 125 gpm of slurry was used. For example, in Run VAA022 (Table 22-2) SO_2 removal by the venturi alone was 33 percent (determined by turning off the spray tower slurry flow for 30 minutes at the end of the test) at 20,000 acfm gas rate and about 2000 ppm adipic acid in venturi liquor. This removal was certainly not insignificant compared to the overall removal of 94.7 percent.

Figure 22-3 is a plot of the SO_2 removal as a function of spray tower adipic acid concentration and spray tower liquid-to-gas ratio for runs with high inlet SO_2 concentration. The SO_2 removals in Figure 22-3 include the effect of the venturi scrubber as mentioned above. As can be seen, the SO_2 removal is more sensitive to spray tower L/G and adipic acid concentration at lower L/G.

Because of the significant effect on the overall SO_2 removal by the venturi, no attempt was made to correlate the data.

22.3.2 Testing with Venturi and Spray Tower in Two-loop Configuration--Test Groups (1) and (3)

For all of these tests, the slurry flow rate to the venturi was held constant at 600 gpm and the venturi plug position was varied according to the gas rate to maintain a constant gas pressure drop of 9 inches H_2O. Variations in the spray tower slurry flow rate and gas rate resulted in a spray tower L/G range of 28 to 100 gal/mcf. The limestone stoichiometry in the spray tower was controlled at 1.7 mole Ca/mole SO_2 absorbed.

Test results indicated that there was insignificant difference in the overall SO_2 removals between runs in Test Group (1) made with open-liquor-loop operation without forced oxidation and runs in Test Group (3) made with closed-liquor-

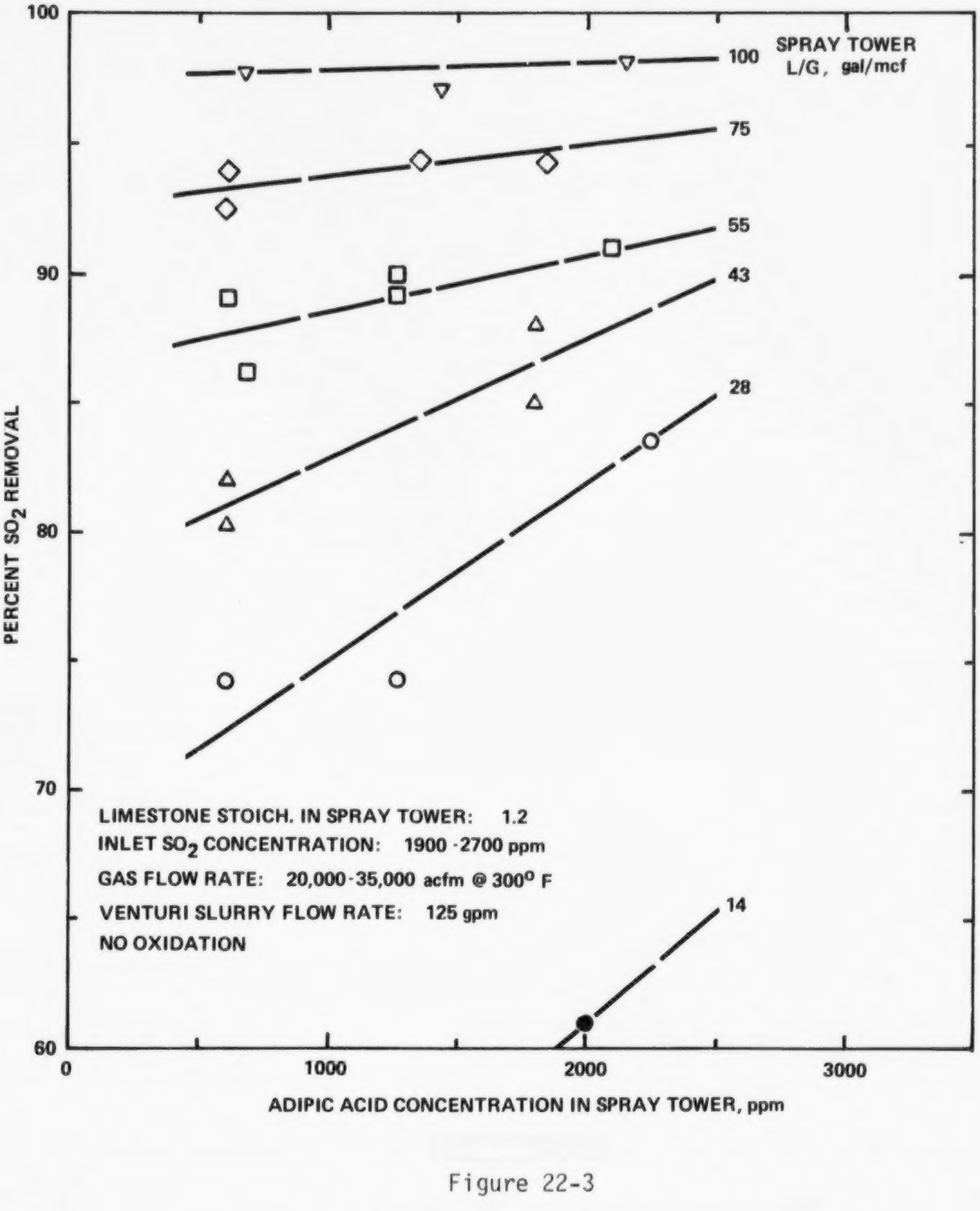


Figure 22-3

Effect Of Adipic Acid Concentration And Spray Tower L/G On SO_2 Removal In The Spray Tower (Minimum Venturi Effect) loop and forced oxidation. Open-liquor-loop tests require a much higher adipic acid addition rate, and since no spent liquor is returned to the scrubbing loops from the dewatering system the adipic acid in the scrubbing loops should be relatively "fresh" and not degraded to any significant degree. Closed-liquor-loop tests combined with forced oxidation, on the other hand, provide the highest concentration of "degraded" adipic acid. In theory, however, the lower-carbon carboxylic acids (such as valeric acid, butyric acid, etc.) produced by the degradation and decomposition of adipic acid should also provide effective buffer capacity.

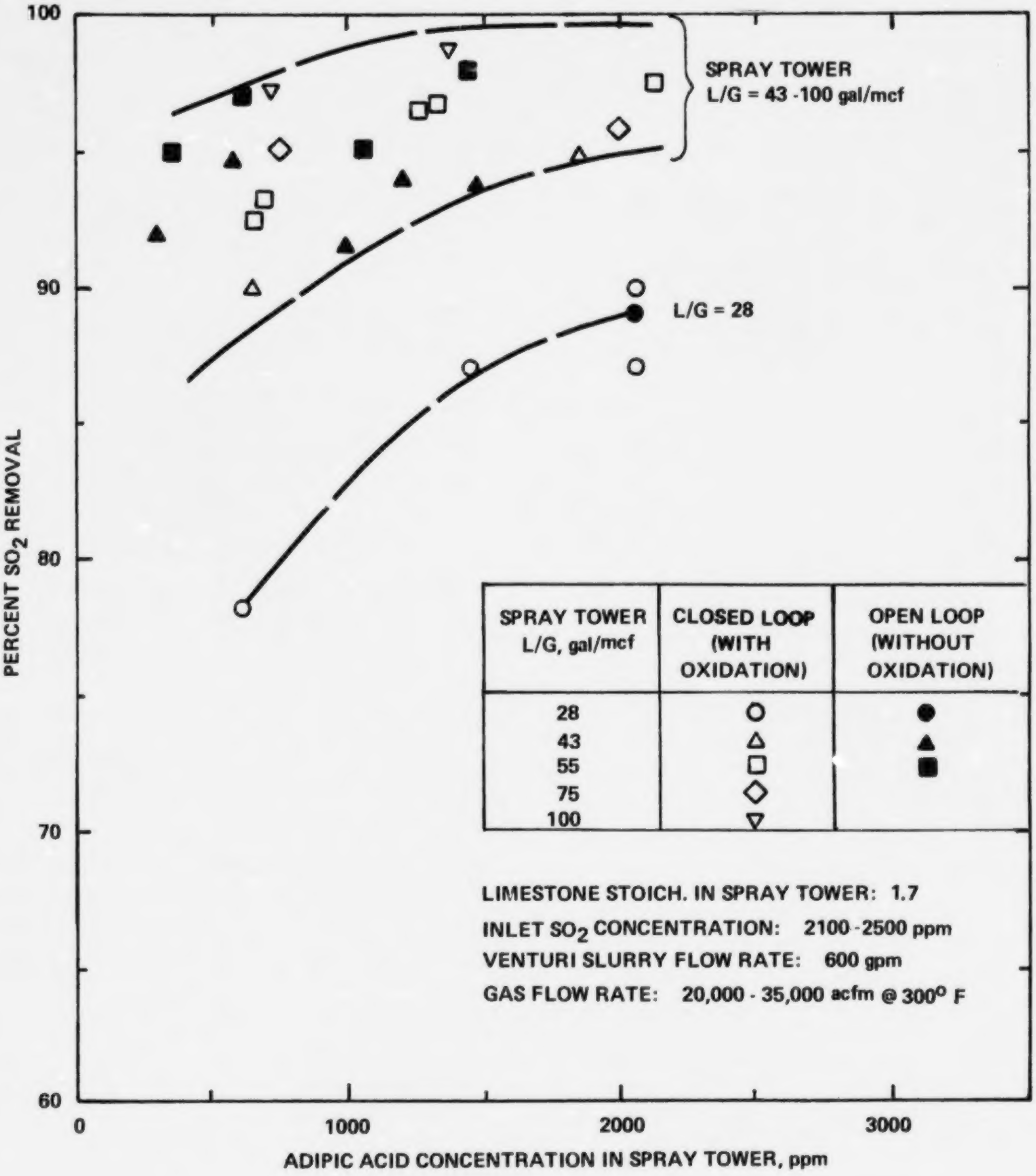
Figure 22-4 shows the SO_2 removal for runs with high inlet SO_2 concentrations as a function of adipic acid concentration and L/G in the spray tower. For spray tower L/G greater than 43 gal/mcf, SO_2 removals were all above 90 percent for spray tower adipic acid concentrations as low as 300 ppm. As in spray tower-only operation (Figure 22-3), SO_2 removal was sensitive to both L/G and adipic acid concentration in the spray tower at a low L/G of 28 gal/mcf.

No correlation of the data was attempted because of the high SO_2 removals (greater than 90 percent) for a wide range of spray tower L/G from 43 to 100 gal/mcf (Figure 22-4).

For runs with low inlet SO_2 concentrations (Table 22-3), SO_2 removals were higher at 93 to 97 percent at 600 ppm adipic acid concentration and L/G of 43 to 100 gal/mcf in the spray tower.

22.4 VENTURI/SPRAY TOWER WITH LIMESTONE/ADIPIC ACID AND ONE-SCRUBBER-LOOP WITHOUT FORCED-OXIDATION

A series of 50 limestone/adipic acid partial factorial tests, Runs VAA201 through VAA250, was conducted on the venturi/spray tower system from late-



LIMESTONE STOICH. IN SPRAY TOWER: 1.7

INLET SO_2 CONCENTRATION: 2100 - 2500 ppm

VENTURI SLURRY FLOW RATE: 600 gpm

GAS FLOW RATE: 20,000 - 35,000 acfm @ 300° F

Figure 22-4

Effect Of Adipic Acid Concentration And Spray Tower L/G On SO_2 Removal In The Venturi/Spray Tower System

October to mid-December 1979. All tests were made without forced oxidation and with a common effluent hold tank for both the venturi and the spray tower as shown in Figure 7-1.

Ten of these tests, Runs VAA201 through VAA206 and Runs VAA234 through VAA237, were venturi/spray tower runs for which the venturi was operated at a constant slurry flow rate of 600 gpm and a pressure drop of 9 inches H_2O. The other 40 tests were spray tower-only runs with the venturi at minimum operating conditions (minimum controllable slurry flow rate of 125 gpm for flue gas cooling and minimum pressure drop of 2 to 4 inches H_2O). The flue gas flow rate was 35,000 acfm @ 300°F for all runs, except for one run (Run VAA207 at 20,000 acfm @ 300°F).

The tests examined the effect of spray tower liquid-to-gas ratio, scrubber inlet liquor pH, and adipic acid concentration on SO_2 removal. Table 22-4 summarizes the test results. The operating conditions held constant during these tests were:

Fly ash loading:	High (2-7 grains/dry scf)
Flue gas rate:	35,000 acfm @ 300°F (except Run VAA207 @ 20,000 acfm)
Hold tank level:	8 ft 6 in. (9.1 - 38 minutes residence time)
Slurry solids concentration:	15 percent
Venturi pressure drop:	9 inches H_2O for runs with 600 gpm, plug wide open for runs with 125 gpm
Spray header configuration (top header is No. 4):	For 400 gpm----Header 4 For 800 gpm----Headers 3 and 4 For 1200 gpm----Headers 2, 3, and 4 For 1600 gpm----All four headers
Solids dewatering equipment:	Clarifier and centrifuge

Each of the four spray headers (spaced 4 ft apart) had seven Bete No. ST48FCN nozzles. The top three headers sprayed the slurry downward while the bottom header sprayed upward.

Table 22-4

RESULTS OF LIMESTONE/ADIPIC ACID FACTORIAL TESTS ON THE ONE-SCRUBBER-LOOP VENTURI/SPRAY TOWER WITHOUT FORCED OXIDATION

Run No.	Liquor Rate (gpm)		ST L/G (gal/mcf)	Pressure Drop (inch H_2O)		Inlet Liquor pH	Outlet Liquor pH	Ave $AD^=$ Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Venturi SO_2 Removal	Replicate
	Venturi	ST		Venturi	Total					Range	Ave.	Range	Ave.		
VAA201	600	1200	43	8.9	13.5	5.70	5.5	710	2410	1880-2120	2005	90-95	93.1	-	A
VAA202	600	800	29	8.7	14.4	5.45	5.2	640	2880	1760-2000	1850	79-84	81.6	45.5	B
VAA203	600	400	15	8.8	13.6	5.85	5.6	590	1240	1680-1840	1760	73-76	74.4	-	
VAA204	600	1600	57	8.9	14.1	5.75	5.4	690	1850	1480-1520	1505	95-96	95.8	-	
VAA205	600	800	29	8.9	15.0	5.80	5.6	650	1910	1560-1600	1570	86-91	88.9	-	B
VAA206	600	1200	43	8.7	14.6	5.65	5.5	680	2710	1760-1880	1850	84-90	86.4	-	A
VAA207	125	1200	75(1)	0.9	3.1	5.75	5.6	570	1740	2000-2080	2045	92-93	92.4	-	
VAA208	125	800	29	2.3	7.7	5.85	5.6	610	1810	1840-1980	1910	72-80	76.4	-	C
VAA209	125	1200	43	3.1	7.9	5.70	5.4	550	1720	2120-2160	2150	77-78	77.9	-	D
VAA210	125	400	15	2.4	7.0	5.80	5.5	620	1880	1600-1760	1715	53-58	54.7	20.6	
VAA211	125	1600	57	3.7	8.8	5.85	5.6	730	1860	1740-2100	1920	87-88	87.3	-	
VAA212	125	1200	43	2.6	7.9	5.60	5.3	650	2080	1760-2000	1835	79-83	80.7	-	D
VAA213	125	800	29	2.5	7.7	5.65	5.5	660	1600	1840-2000	1965	69-74	72.1	17.6	C
VAA214	125	1200	43	3.1	8.6	5.35	5.0	660	2170	1800-2200	2010	68-76	71.4	-	
VAA215	125	1200	43	2.7	9.0	5.05	-	610	2120	1760-2200	2115	57-65	60.5	-	E
VAA216	125	1200	43	2.7	8.1	4.65	5.2	660	1810	1800-2000	1900	44-50	46.0	-	
VAA217	125	1600	57	2.7	7.7	5.35	5.6	590	2170	1720-2000	1855	71-83	79.2	-	
VAA218	125	1600	57	2.3	7.6	5.00	4.7	660	2280	2080-2280	2165	54-63	58.3	-	
VAA219	125	1200	43	2.6	8.0	5.00	-	710	2240	1760-2160	1940	56-62	58.0	-	E
VAA220	125	1600	57	2.7	7.4	4.55	-	840	2310	2040-2080	2075	36-42	40.3	-	
VAA221	125	800	29	1.9	8.6	5.50	-	1170	2640	1880-2000	1910	72-76	75.2	-	F
VAA222	125	400	15	3.3	7.9	5.50	-	1290	3250	1960-2000	1985	55-61	57.9	21.9	G
VAA223	125	1200	43	3.0	7.8	5.40	5.4	1370	3080	1800-2080	1945	83-88	86.5	-	
VAA224	125	1600	57	3.4	8.2	5.50	-	1190	3120	1920-2060	1900	91-93	92.6	-	
VAA225	125	800	29	3.1	7.9	5.45	5.3	1190	2930	1720-1920	1840	79-83	81.2	-	F
VAA226	125	400	15	4.0	9.0	5.60	-	1280	4050	1740-2040	1880	63-66	64.6	-	G
VAA227	125	1200	43	3.1	8.0	5.40	-	1270	2900	1400-1680	1595	87-91	89.8	-	
VAA228	125	1200	43	3.6	8.9	4.90	-	1450	2990	1880-2040	1930	66-70	69.2	-	H
VAA229	125	1200	43	3.7	8.9	4.70	-	1380	3370	1640-1780	1735	50-55	51.9	-	
VAA230	125	800	29	4.6	9.7	5.45	-	1350	3470	1880-2000	1970	69-80	77.7	-	
VAA231	125	800	29	4.1	9.6	5.05	-	1340	3240	1740-2200	1900	59-72	64.9	21.6	
VAA232	125	1200	43	4.2	8.9	5.00	-	1410	4410	2260-2560	2400	69-80	74.7	-	H
VAA233	125	800	29	3.9	8.9	4.65	-	1400	3700	1720-1880	1780	45-50	48.4	-	
VAA234	600	800	29	9.0	14.0	5.20	-	1300	4170	2000-2200	2155	85-90	87.4	51.9	I
VAA235	600	400	15	9.2	15.2	5.45	-	1350	4030	1520-1800	1640	84-89	85.8	58.0	
VAA236	600	1200	43	8.9	12.2	5.35	-	1410	4180	1960-2240	2145	95-97	95.9	-	
VAA237	600	800	29	9.0	11.3	5.40	-	1290	4260	1860-2040	1915	93-94	93.6	-	I
VAA238	125	800	29	3.1	8.1	5.30	-	2310	4580	2480-2720	2625	84-90	88.3	39.4	J
VAA239	125	1200	43	3.2	8.1	5.65	-	1980	4110	2340-2520	2415	96-97	96.5	42.4	K
VAA240	125	400	15	3.7	8.5	5.25	4.8	1900	4000	2800-3000	2935	68-71	69.3	46.0	L
VAA241	125	1600	57	3.7	9.3	5.35	4.9	1810	3760	1840-2240	2025	96-97	96.6	-	
VAA242	125	800	29	3.1	7.6	5.65	-	2070	3930	2240-2400	2340	93-95	94.3	-	J
VAA243	125	1200	43	2.9	7.7	5.60	-	2040	3850	2360-2480	2430	96-97	96.8	-	K
VAA244	125	400	15	3.8	8.6	5.45	4.8	2300	5030	2200-2600	2480	68-72	69.5	-	L
VAA245	125	800	29	3.0	7.5	5.40	-	2260	3690	2360-2640	2440	91-93	92.1	-	
VAA246	125	800	28	3.0	7.9	5.05	-	2370	3850	1800-2160	1900	87-93	89.9	-	
VAA247	125	800	29	3.8	9.0	4.60	4.5	2170	4010	2660-2880	2810	60-66	63.5	-	
VAA248	125	1200	43	2.9	7.7	5.50	-	2000	3620	1840-2160	1980	96-98	96.8	-	
VAA249	125	1200	43	3.0	7.7	5.00	-	2270	4640	2180-2360	2245	90-93	91.7	-	
VAA250	125	1200	43	3.8	9.2	4.55	4.2	2210	4440	2300-2560	2470	69-73	71.3	-	

(1) Flue gas rate = 20,000 acfm @ 300°F for Run VAA 207.
All other runs at 35,000 acfm @ 300°F.

22.4.1 Overall SO_2 Removal by the Venturi and Spray Tower

Equation 22-8 for predicting SO_2 removal has been fitted to the 10 venturi/spray tower runs (Runs VAA201 through VAA206 and VAA234 through VAA237) for which the slurry flow rate to the venturi was held at 600 gpm and the venturi pressure drop was 9 inches H_2O.

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left[-0.0019\,(L/G)^{0.55}\,\exp(0.8\text{pH} + 8\times10^{-4}\,A)\right] \quad (22\text{-}8)$$

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = scrubber inlet liquor pH
A = adipic acid concentration in scrubber liquor, ppm

The ranges of operating variables covered by the 10 correlated runs are:

L/G = 15-57 gal/mcf
pH = 5.2-5.8 (limestone stoichiometry controlled at 1.2)
A = 600-1400 ppm
Gas flow rate = 35,000 acfm at 300°F
Inlet SO_2 concentration = 1500-2200 ppm
Venturi liquid-to-gas ratio = 21 gal/mcf
Venturi pressure drop = 9 inches H_2O

Equation 22-8 explains 90 percent of the variation in the data for SO_2 removal with a standard error of estimate of 2.7 percent SO_2 removal.

22.4.2 SO_2 Removal by Spray Tower With Minimum Venturi Effect

Equation 22-9 for prediction of SO_2 removal has been fitted to the 40 spray tower runs (minimum effect of venturi, with 125 gpm for flue gas humidification):

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left[-2.2\times10^{-4}\,(L/G)^{0.75}\,\exp(\text{pH} + 6.2\times10^{-4}\,A)\right] \quad (22\text{-}9)$$

where L/G, pH, and A have the same definition as for Equation 22-8.

The ranges of variables covered by the 40 correlated runs are:

L/G = 15-75 gal/mcf
pH = 4.6-5.9
A = 600-2400 ppm
Gas flow rate = 35,000 acfm at 300°F (one test at 20,000 acfm)
Inlet SO_2 concentration = 1600-2900 ppm
Venturi slurry flow rate = 125 gpm
Venturi pressure drop = 2-4 inches H_2O (wide open plug)

Equation 22-9 explains 93 percent of the variation in the data for SO_2 removal with a standard error of estimate of 4.3 percent SO_2 removal.

It is important to note that the SO_2 removal predicted by Equation 22-9 includes the effect of the venturi operating at the minimum conditions defined above. The magnitude of this effect is discussed later.

Figures 22-5 through 22-7 illustrate the effects of spray tower liquid-to-gas ratio and inlet liquor pH on SO_2 removal at adipic acid concentrations of 600, 1300, and 2000 ppm, respectively. The lines on the figures represent the predictions of Equation 22-9 with actual data points also shown.

Note that the SO_2 removals for a pH of 4.6 and 2000 ppm adipic acid in Figure 22-7 are similar both to those in Figure 22-6 for a pH of 5.0 and 1300 ppm adipic acid, and to those in Figure 22-5 for a pH of 5.4 and 600 ppm adipic acid. These values are more clearly seen in the following table:

		Percent SO_2 Removal at Spray Tower L/G of		
Scrubber Inlet pH	Adipic Acid, ppm	30 gal/mcf	50 gal/mcf	70 gal/mcf
5.4	600	60	74	82
5.0	1300	61	75	83
4.6	2000	62	76	84

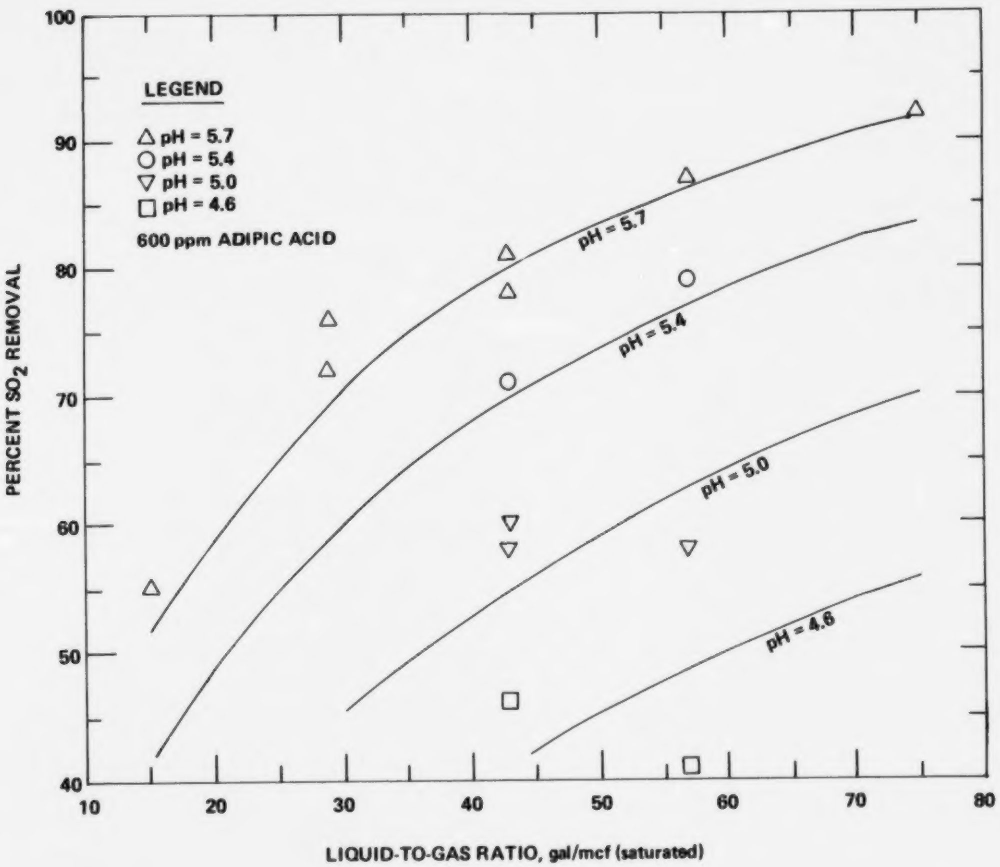


Figure 22-5. Effect Of Spray Tower Liquid-To-Gas Ratio And Inlet pH On Spray Tower SO_2 Removal At 600 ppm Adipic Acid (Minimum Venturi Effect)

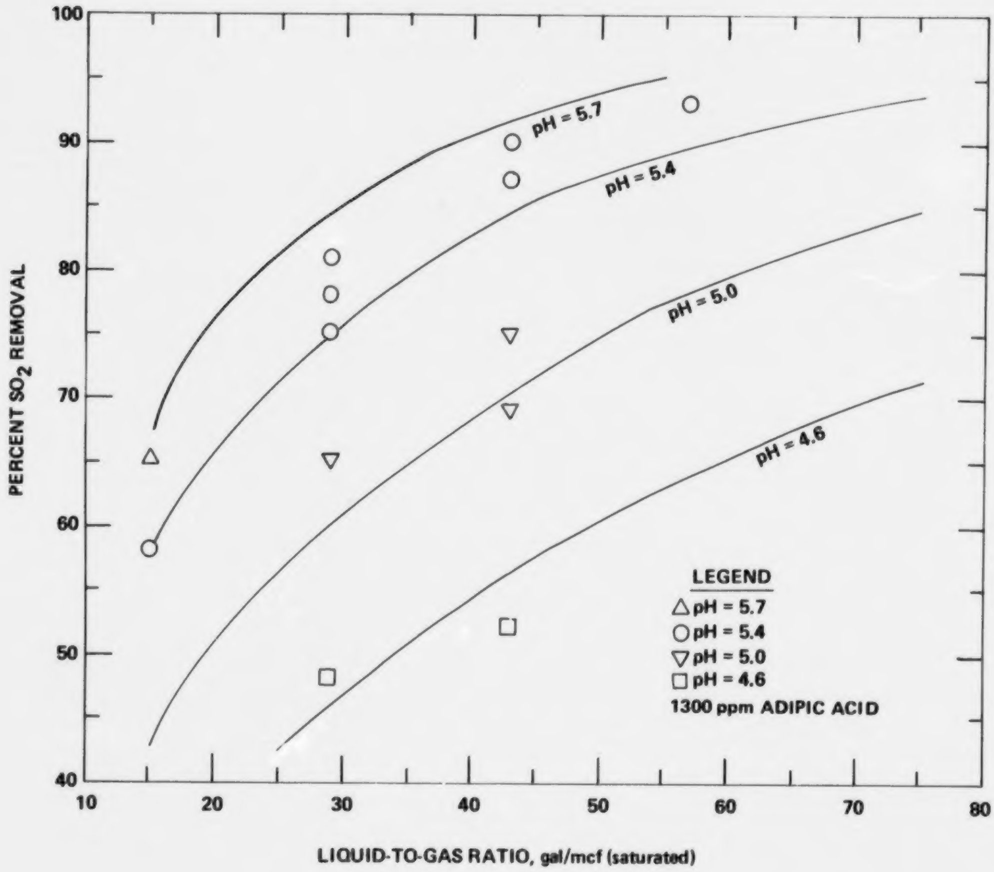


Figure 22-6. Effect Of Spray Tower Liquid-To-Gas Ratio And Inlet pH On Spray Tower SO_2 Removal At 1300 ppm Adipic Acid (Minimum Venturi Effect)

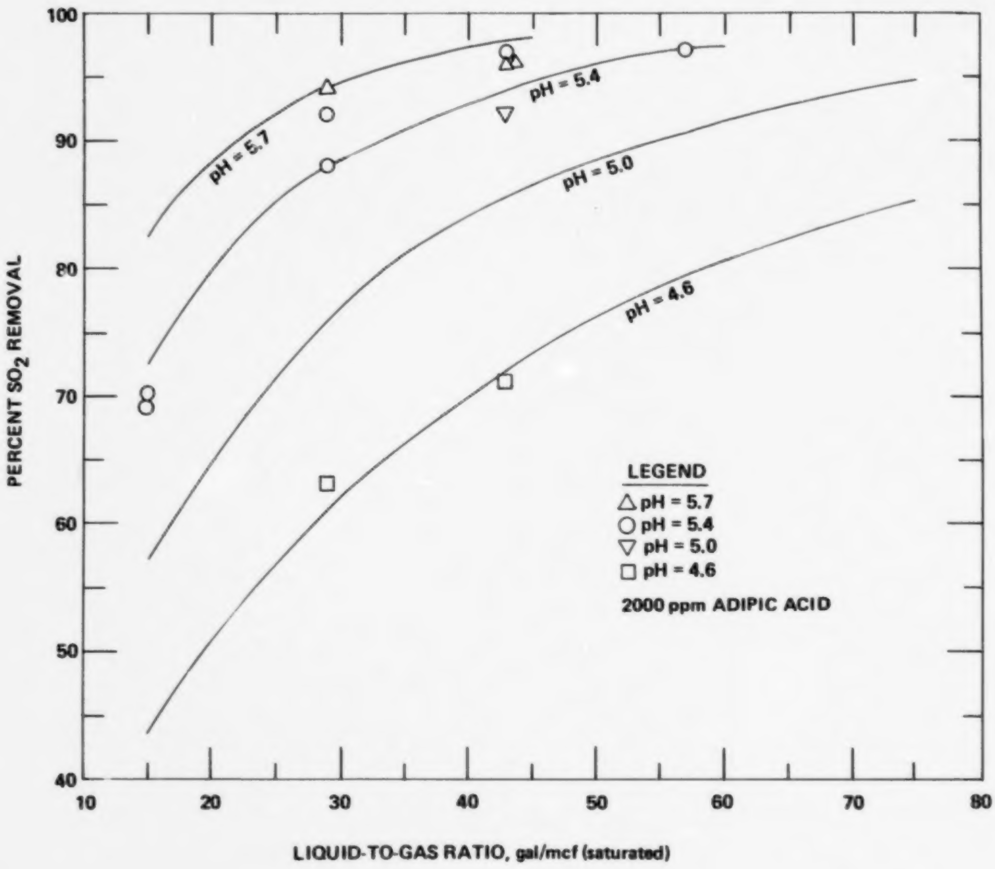


Figure 22-7. Effect Of Spray Tower Liquid-To-Gas Ratio And Inlet pH On Spray Tower SO_2 Removal At 2000 ppm Adipic Acid (Minimum Venturi Effect)

Thus, within the ranges tested, each 0.4 unit drop in scrubber inlet pH requires a 700 ppm increase in adipic acid concentration to achieve a similar percent SO_2 removal.

22.4.3 SO_2 Removal by Venturi Alone at Minimum Slurry Flow Rate and Pressure Drop

For a 2 to 4-hour period at the end of each of seven factorial tests with the spray tower alone (Runs VAA210, VAA213, VAA222, VAA231, VAA238, VAA239, and VAA240), the spray tower slurry flow was shut off in order to determine the SO_2 removal achieved by the venturi alone at a minimum slurry flow rate of 125 gpm, minimum pressure drop of 2 to 4 inches H_2O (plug wide open), and 35,000 acfm gas flow rate (venturi L/G = 4.5 gal/mcf).

These tests indicated that the venturi scrubber obtains about 20 percent SO_2 removal at 600 ppm adipic acid concentration and an inlet pH of 5.7, 22 percent SO_2 removal at 1300 ppm adipic acid and a pH of 5.3, and 42 percent SO_2 removal at 2000 ppm adipic acid and a pH of 5.4

Equation 22-9 does not include any corrections for SO_2 removal in the venturi. This should be taken into consideration when using Equation 22-9 with Figures 22-5 through 22-7.

22.5 SPRAY TOWER ONLY WITH LIMESTONE AND ONE-SCRUBBER-LOOP WITH AND WITHOUT FORCED-OXIDATION

The venturi scrubber was physically removed from Train 100 in June 1980 to allow testing with a true spray tower-only configuration. Before this modification, the effect of the venturi in spray tower-only testing could not be avoided, even at the minimum venturi slurry flow rate and pressure drop (see Sections 22.3.1, 22.4.2, and 22.4.3).

Four series of limestone factorial tests (Series SXX100, SXX200, SXX300, and SXX400) were conducted after the removal of the venturi from mid-June through mid-October 1980. All tests were made without adipic acid.

The first two series (Series SXX100 and SXX200) were made with a maximum slurry flow rate of 1600 gpm (400 gpm/header, 7 spray nozzles/header). Series SXX100 was made with one tank without forced oxidation, while Series SXX200 was with two tanks and forced oxidation.

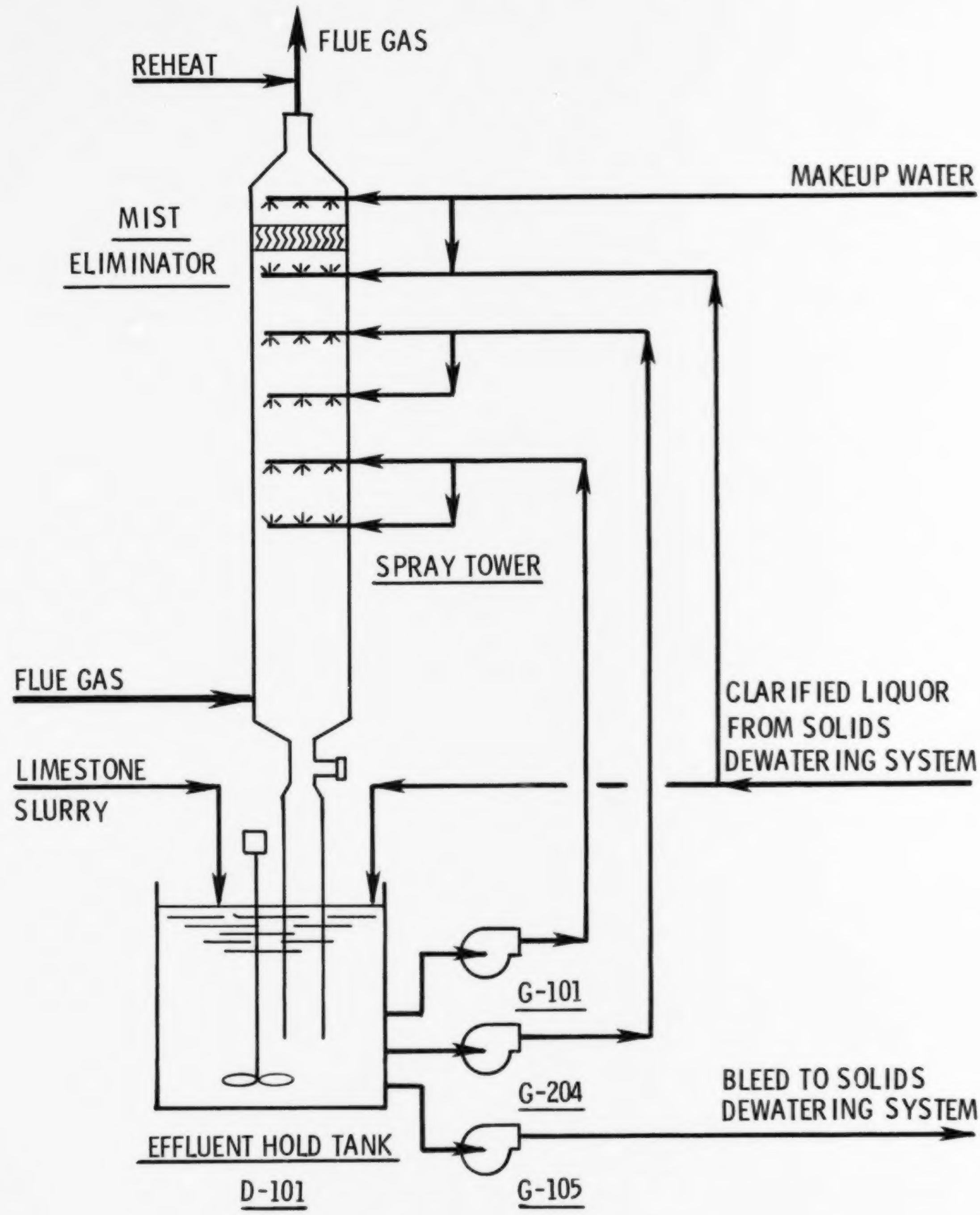
In mid-August 1980, the spray tower external piping and the spray header assembly were modified to increase the maximum slurry flow rate from 1600 to 2400 gpm. Series SXX300 and SXX400 were conducted after this modification with the maximum 2400 gpm slurry rate (600 gpm/header, 12 nozzles/header). These were again made with one tank without forced oxidation (Series SXX300), and two tanks with forced oxidation (Series SXX400).

In all four series the effects of gas and slurry flow rates (or liquid-to-gas ratio) and scrubber inlet pH on SO_2 removal were examined.

22.5.1 Limestone Tests with One Tank without Forced-oxidation at 1600 gpm Maximum Slurry Rate

Twenty-one runs (Runs SXX101 through SXX121) were made using limestone without adipic acid, with a single tank without forced oxidation as shown in Figure 22-8. The operating conditions common to these tests were:

Fly ash loading: High (2 to 7 grains/dry scf)
Slurry solids concentration: 15 percent
Effluent hold tank level: 8.5 ft
Effluent hold tank residence time: 12.5 to 50 minutes
Solids dewatering equipment: Clarifier and centrifuge
Spray header configuration (top header is No. 4):
- For 400 gpm----Header 4
- For 800 gpm----Headers 3 and 4
- For 1200 gpm----Headers 2, 3, and 4
- For 1600 gpm----All four headers



FLUE GAS
REHEAT
MAKEUP WATER
MIST ELIMINATOR
SPRAY TOWER
FLUE GAS
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
LIMESTONE SLURRY
G-101
G-204
BLEED TO SOLIDS DEWATERING SYSTEM
EFFLUENT HOLD TANK
D-101
G-105

Figure 22-8

Spray Tower-Only Configuration Using A Single Tank
Without Forced Oxidation
(1600 gpm Maximum Slurry Flow Rate)

Each of the four spray headers (spaced 4 ft apart) had seven Bete No. ST48FCN nozzles. The top three headers sprayed downward while the bottom header sprayed upward.

Table 22-5 summarizes the results of the 21 runs. The spray tower inlet pH was controlled at three levels of 5.0 (actual 5.1), 5.4, and 5.8. For the pH 5.8 runs, a limestone stoichiometry override of 1.3 moles Ca/mole SO_2 absorbed was imposed, but this value was seldom exceeded.

Equation 22-10 for predicting SO_2 removal has been fitted to the 21 run-averaged data points (Table 22-5):

$$\underset{\text{Removal}}{\text{Fraction } SO_2} = 1-\exp[-4.4\times10^{-4}\ (L/G)^{0.71} \exp(0.84\ pH)] \qquad (22\text{-}10)$$

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = spray tower inlet liquor pH

The ranges of operating variables covered by the 21 correlated runs are:

Liquid-to-gas ratio = 14-100 gal/mcf
pH = 5.0-5.85
Gas flow rate = 20,000-35,000 acfm at 300°F
Slurry flow rate = 400-1600 gpm (400 gpm per header)
Inlet SO_2 concentration = 2000-2500 ppm
Sulfite oxidation = 10-35 percent

Equation 22-10 explains 97 percent of the variation in the data for SO_2 removal with a standard error of estimate of 2.5 percent SO_2 removal.

Figure 22-9 is a plot of SO_2 removal as a function of spray tower liquid-to-gas ratio with inlet pH as a parameter. The curves on the figure represent the predictions of Equation 22-10. For a given value of L/G, SO_2 removal at pH

Table 22-5

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS WITH ONE TANK AND WITHOUT FORCED OXIDATION AT 1600 GPM MAXIMUM SLURRY RATE

Run No.	Gas Rate @ 300° F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Sulfite Oxid. (%)	Replicate
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.		
SXX-101	20,000	1592	100	--	.16	4.99-5.37	5.15	4.90	1085	1880 - 2120	2005	59-66	61.6	32.6	D
SXX-102	27,500	1592	72	--	.24	4.99-5.18	5.05	4.75	1005	1920 - 2120	2055	48-54	49.4	33.6	A
SXX-103	35,000	1588	57	--	.38	4.85-5.20	5.00	4.75	995	2240 - 2400	2310	37-41	38.9	34.8	G
SXX-104	27,500	1589	72	--	.26	5.00-5.07	5.05	4.75	990	2040 - 2280	2175	43-48	45.0	28.6	A
SXX-105	20,000	1596	100	--	.16	5.33-5.47	5.40	5.20	1005	2240 - 2320	2275	66-68	67.3	17.9	B
SXX-106	27,500	1587	72	--	.32	5.33-5.55	5.50	5.10	1210	2240 - 2300	2265	55-65	59.1	21.7	
SXX-107	35,000	1596	57	3.6	.38	5.39-5.55	5.45	4.90	2040	2080 - 2200	2100	52-57	54.5	22.5	F
SXX-108	20,000	1592	100	1.3	.18	5.34-5.47	5.40	5.00	2130	1920 - 2160	2015	66-71	68.5	19.3	B
SXX-109	35,000	790	28	--	.39	5.35-5.50	5.40	4.95	1320	2000 - 2240	2135	39-44	41.1	18.1	
SXX-110	20,000	1201	75	1.3	.20	5.36-5.44	5.40	5.00	1785	2080 - 2240	2135	55-61	58.4	19.8	
SXX-111	27,500	1198	54	1.9	.25	5.39-5.55	5.45	5.05	1795	1960 - 2160	2010	48-51	50.5	7.8	
SXX-112	35,000	1595	57	2.7	.39	5.70-5.81	5.75	5.40	1640	2040 - 2320	2200	60-62	60.9	28.3	C
SXX-113	27,500	1586	72	1.9	.25	5.63-5.94	5.80	5.45	1245	2400 - 2600	2475	67-70	68.2	13.2	
SXX-114	20,000	1588	99	1.4	.18	5.75-5.97	5.85	5.50	1115	2120 - 2440	2315	76-81	78.8	19.6	E
SXX-115	35,000	1590	57	3.0	.38	5.58-5.94	5.75	5.30	1390	2040 - 2680	2480	55-65	60.4	12.7	C
SXX-116	35,000	796	28	2.4	.39	5.72-5.99	5.85	5.35	1555	2000 - 2160	2130	48-50	49.6	19.0	
SXX-117	35,000	393	14	2.5	.38	5.84-5.89	5.85	5.30	1680	2040 - 2240	2110	27-32	30.6	10.8	
SXX-118	20,000	1588	99	1.3	.17	5.07-5.14	5.10	4.75	1930	2440 - 2680	2565	55-61	57.9	28.7	D
SXX-119	20,000	1594	100	1.3	.18	5.72-5.88	5.80	5.45	1735	2200 - 2520	2370	77-85	81.2	34.2	E
SXX-120	35,000	1596	57	3.0	.39	5.29-5.49	5.40	5.00	2135	2200 - 2360	2315	47-54	49.5	25.6	F
SXX-121	35,000	1587	57	2.8	.39	4.96-5.17	5.05	5.15	1910	2000 - 2440	2250	30-43	39.8	28.5	G

* Δ P between taps in front of presaturator and after Mist Eliminator (M.E.)

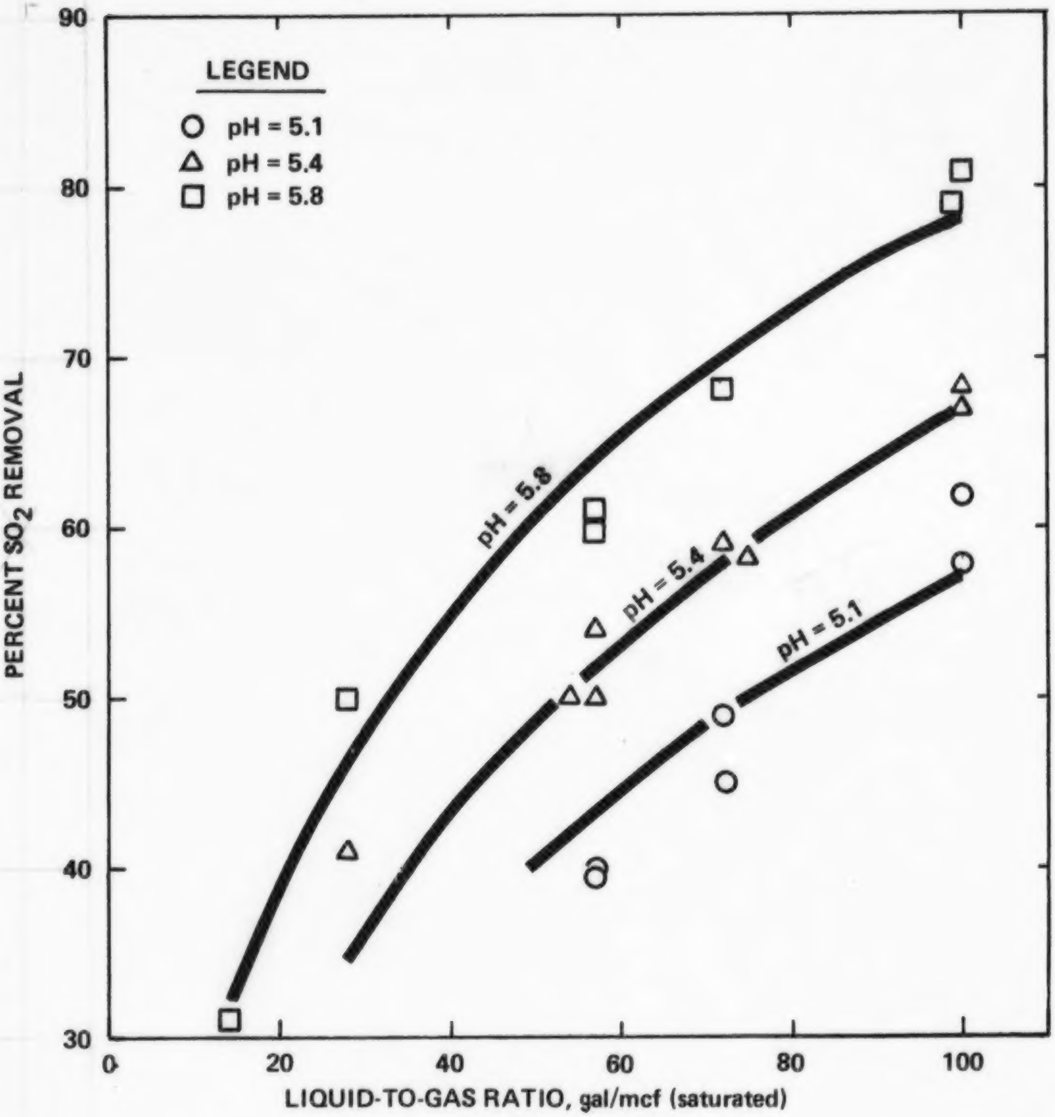


Figure 22-9

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal Without Forced Oxidation And Without Adipic Acid (1600 gpm Maximum Slurry Rate)

5.8 is about 12 percentage points higher than for pH 5.4, and about 21 percentage points higher than for pH 5.1.

22.5.2 Limestone Tests with Two-tank Forced-Oxidation at 1600 gpm Maximum Slurry Rate

Thirty-seven limestone runs, including seven repeated runs, were made without adipic acid and with two-tank forced oxidation as shown in Figure 22-10.

Low sulfur coal was burned in Boiler No. 10 during nine of the 37 runs. Tables 22-6 and 22-7 list separately the test results with high and low sulfur coals, respectively. The operating conditions common to all tests were:

Fly ash loading: High (2 to 7 grains/dry scf)
Slurry solids concentration: 15 percent
Oxidation tank level: 18 ft (4.2 to 8.4 minutes residence time)
Effluent hold tank level: 8.5 ft (12.5 to 25 minutes residence time)
Air flow rate to oxidizer: 250 scfm
Solids dewatering equipment: Clarifier and centrifuge
Spray header configuration (top header is No. 4): For 800 gpm----Headers 3 and 4
For 1200 gpm----Headers 2, 3, and 4
For 1600 gpm----All four headers

Each of the four spray headers (spaced 4 ft apart) had seven Bete No. ST48FCN nozzles. The top three headers sprayed downward while the bottom header sprayed upward. As in the factorial tests without forced oxidation (see Section 22.5.1), the spray tower inlet pH was controlled at three levels of 5.0, 5.4, and 5.8.

Equation 22-11 for predicting SO_2 removal has been fitted to 27 run-averaged data points in Table 22-6. Run SXX217(R) was not included in the correlation due to higher than normal inlet SO_2 concentration.

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp[-0.0042(L/G)^{0.73} \exp(0.47\ pH)] \qquad (22\text{-}11)$$

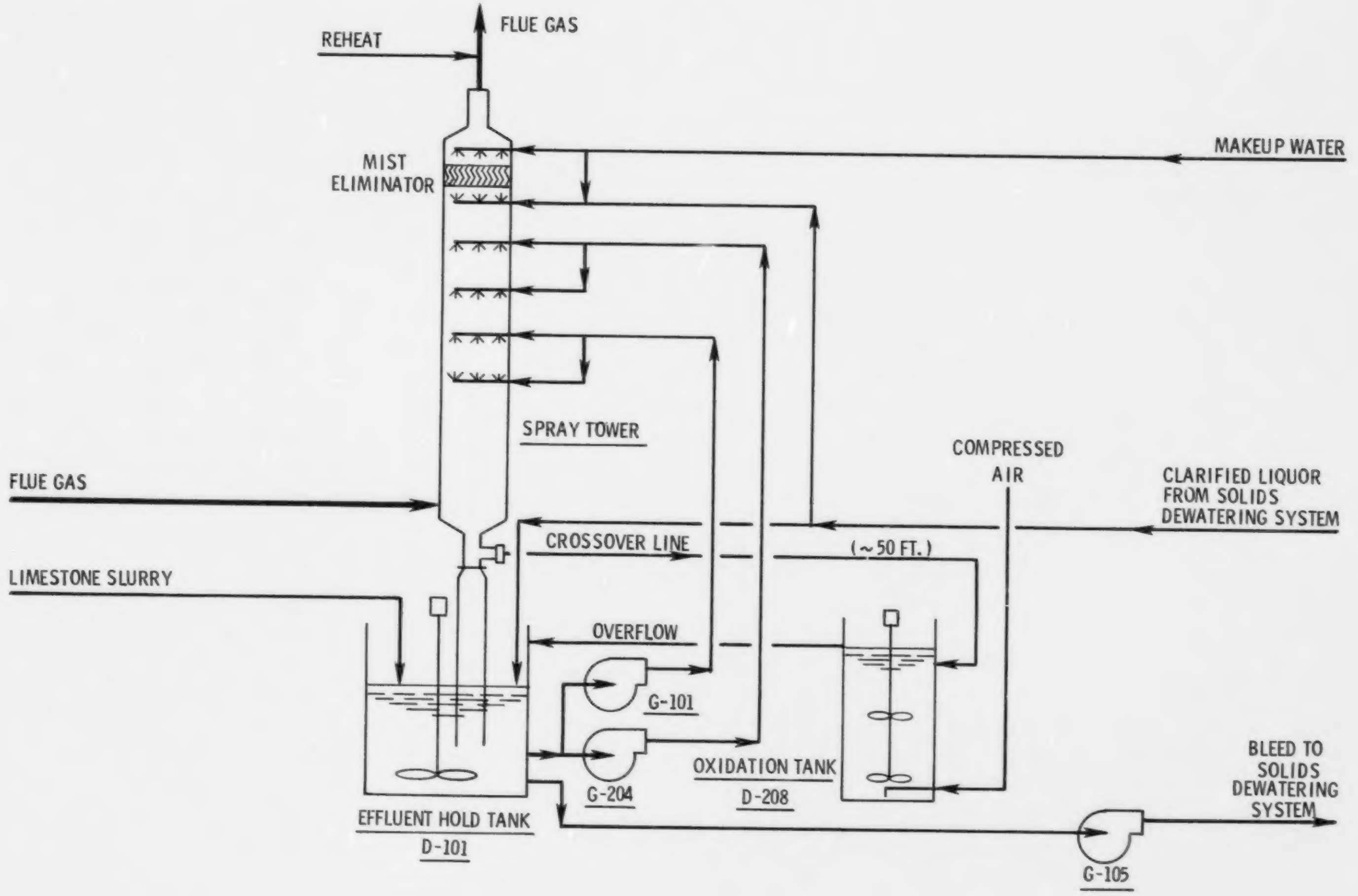

REHEAT
FLUE GAS
MIST ELIMINATOR
MAKEUP WATER
SPRAY TOWER
FLUE GAS
COMPRESSED AIR
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
CROSSOVER LINE
(~50 FT.)
LIMESTONE SLURRY
OVERFLOW
G-101
G-204
OXIDATION TANK
D-208
EFFLUENT HOLD TANK
D-101
BLEED TO SOLIDS DEWATERING SYSTEM
G-105

Figure 22-10

Spray Tower-Only Configuration Using
Two Tanks With Forced Oxidation
(1600 gpm Maximum Slurry Rate)

Table 22-6

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS USING TWO TANKS WITH FORCED OXIDATION AT 1600 GPM MAXIMUM SLURRY RATE

Run No.	Gas Rate @ 300° F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Sulfite** Oxid. (%)	Replicate
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.		
SXX-201	20,000	1600	100	1.2	.19	4.90-5.10	5.00	4.18	2875	2200 - 2360	2245	67-72	70.2	99.4	A
SXX-201(R)	20,000	1600	100	0.5	.18	5.00-5.10	5.05	3.98	3815	2160 - 2400	2265	73-76	74.2	99.5	A
SXX-202	35,000	1200	43	2.6	.38	5.00-5.05	5.05	4.15	2930	2040 - 2200	2120	49-54	52.0	99.2	
SXX-203	27,500	1600	73	1.8	.27	4.95-5.15	5.05	4.26	2510	2060 - 2210	2130	56-63	58.6	100	B
SXX-203(R)	27,500	1600	73	1.2	.25	4.90-5.10	5.00	4.02	3935	2400 - 2680	2460	62-67	64.4	100	B
SXX-204	35,000	800	28	2.4	.37	5.00-5.10	5.05	4.00	3255	2120 - 2400	2285	41-49	44.3	99.3	
SXX-205(R)	35,000	1600	57	1.9	.38	4.95-5.20	5.10	4.05	3765	2320 - 2480	2405	52-57	54.1	100	
SXX-206	27,500	1600	73	1.8	.24	5.00-5.15	5.05	4.64	3095	2360 - 2680	2520	65-73	69.7	100	B
SXX-207	20,000	1600	100	1.2	.18	4.95-5.10	5.05	4.53	3075	2480 - 2600	2535	75-80	77.9	100	A
SXX-208	20,000	1600	100	0.4	.19	5.40-5.50	5.45	4.88	3850	2200 - 2440	2375	78-81	79.4	100	C
SXX-209	35,000	800	28	2.5	.37	5.35-5.45	5.40	4.76	3265	2400 - 2840	2615	41-48	44.9	99.8	D
SXX-210	35,000	1200	43	1.9	.38	5.35-5.45	5.40	4.62	3680	2000 - 2600	2350	50-58	54.7	99.5	E
SXX-211	27,500	1600	73	1.1	.26	5.45-5.55	5.50	4.83	3905	2360 - 2520	2405	67-72	69.6	100	
SXX-212	35,000	1600	57	2.7	.37	5.25-5.45	5.35	4.47	3830	2440 - 2560	2480	57-65	60.6	99.5	
SXX-213	20,000	1600	100	0.5	.18	5.25-5.45	5.40	4.56	3700	2480 - 2720	2615	76-84	79.3	100	C
SXX-214	35,000	800	28	1.7	.36	5.25-5.45	5.35	4.59	3905	2280 - 2600	2480	42-50	46.0	100	D
SXX-215	20,000	1200	75	0.6	.18	5.30-5.45	5.40	4.68	3770	1920 - 2200	2155	65-69	66.6	99.3	
SXX-215(R)	20,000	1200	75	0.5	.18	5.30-5.45	5.40	4.64	3525	2520 - 2640	2605	67-72	70.4	99.8	
SXX-216(R)	35,000	1200	43	2.1	.36	5.30-5.55	5.40	4.80	3860	2040 - 2680	2450	50-60	55.9	99.8	E
SXX-217	27,500	1200	54	1.8	.25	5.45-5.50	5.45	4.82	3620	2000 - 2520	2250	56-65	59.5	100	G
SXX-217(R)	27,500	1200	54	1.9	.25	5.35-5.50	5.40	4.27	2380	2400 - 2800	2650	43-56	51.5	100	G
SXX-218	35,000	1600	57	2.5	.38	5.75-5.85	5.80	5.12	3580	2240 - 2480	2375	68-71	69.5	100	F
SXX-219	27,500	1600	73	1.9	.28	5.70-5.95	5.85	5.42	3490	2200 - 2480	2325	72-80	77.1	98.8	
SXX-220	35,000	1200	43	2.0	.36	5.70-5.90	5.80	4.80	3255	1960 - 2640	2330	57-69	62.8	100	
SXX-221	20,000	1600	100	1.2	.18	5.55-5.95	5.75	5.37	2930	2280 - 2540	2380	89-92	90.0	100	
SXX-222	35,000	1600	57	2.6	.38	5.80-5.95	5.90	5.23	3460	2280 - 2580	2470	76-79	76.8	99.4	F
SXX-222(R)	35,000	1600	57	2.7	.38	5.70-5.85	5.75	5.28	2780	2320 - 2480	2410	61-63	62.4	100	F
SXX-223	35,000	800	28	1.6	.38	5.75-5.85	5.85	4.91	3480	2200 - 2560	2390	54-59	56.1	99.4	

* ΔP between taps in front of presaturator and after mist eliminator (M.E.)
** All runs with 250 scfm of air to the oxidizer

Table 22-7

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS USING TWO TANKS WITH FORCED OXIDATION AT 1600 GPM MAXIMUM SLURRY RATE -LOW INLET SO_2 CONCENTRATION-

Run No.	Gas Rate @ 300° F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- Conc (ppm)	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Sulfite** Oxid. (%)	Replicate
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.		
SXX-205	35,000	1600	57	2.7	.38	4.90-5.05	4.97	4.03	2390	1520 - 1760	1680	26-35	31.8	99.3	
SXX-216	35,000	1200	43	1.9	.37	5.40-5.45	5.40	4.68	3835	1480 - 1960	1645	50-55	53.4	99.4	
SXX-508	20,000	1600	100	0.5	.18	5.25-5.50	5.34	4.82	3945	1520 - 1840	1680	75-81	78.5	100	A
SXX-509	35,000	800	28	2.2	.36	5.40-5.65	5.53	4.75	4170	1240 - 1500	1365	46-53	48.7	99.8	B
SXX-511	27,500	1600	73	1.1	.26	5.25-5.45	5.37	4.87	3905	1480 - 1720	1620	65-73	70.5	100	
SXX-512	35,000	1600	57	3.0	.37	5.39	5.39	4.95	4085	1600 - 1640	1610	64-65	64.4	100	
SXX-513	20,000	1600	100	0.5	.18	5.35-5.55	5.43	4.71	4015	1480 - 1600	1520	74-78	75.8	99.4	A
SXX-514	35,000	800	28	1.7	.36	5.30-5.45	5.40	4.16	3980	1280 - 1600	1460	44-48	45.2	99.3	B
SXX-517	27,500	1200	54	1.2	.25	5.45-5.55	5.47	4.85	3920	1000 - 1240	1115	64-72	67.3	98.9	

* ΔP between taps in front of presaturator and after mist eliminator (M.E.)

** All runs with 250 scfm of air to the oxidizer

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = spray tower inlet liquor pH

The ranges of operating variables covered by the 27 correlated runs are:

Liquid-to-gas ratio = 28-100 gal/mcf
pH = 5.00-5.90
Gas flow rate = 20,000-35,000 acfm at 300°F
Slurry flow rate = 800-1600 gpm (400 gpm per header)
Inlet SO_2 concentration = 2120-2615 ppm
Sulfite oxidation = 98.8-100 percent

Equation 22-11 explains 91 percent of the variation in the data for SO_2 removal with a standard error of estimate of 3.4 percent SO_2 removal.

Figure 22-11 is a plot of SO_2 removal as a function of spray tower L/G with inlet pH as a parameter. The data points from forced oxidation tests (Runs SXX201 through SXX223 in Table 22-6) are shown together with solid lines predicted from Equation 22-11. For comparison, the corresponding dashed lines as predicted from Equation 22-10 for tests without forced oxidation (Runs SXX101 through SXX121 in Table 22-5) are also shown.

These curves indicate that, for a given L/G and pH, forced oxidation gives a higher SO_2 removal than no forced oxidation. Forced oxidation eliminates bisulfite in the liquid and improves the SO_2 mass transfer. The effect is especially pronounced as the pH is decreased. For example, at a pH of 5.8 and L/G of 100 gal/mcf, running with forced oxidation increased SO_2 removal by 4.5 percentage points from 80.0 to 84.5 percent, whereas at a pH of 5.0 and LG of 100 gal/mcf, forced oxidation improved SO_2 removal by 18 percentage points from 54 to 72 percent.

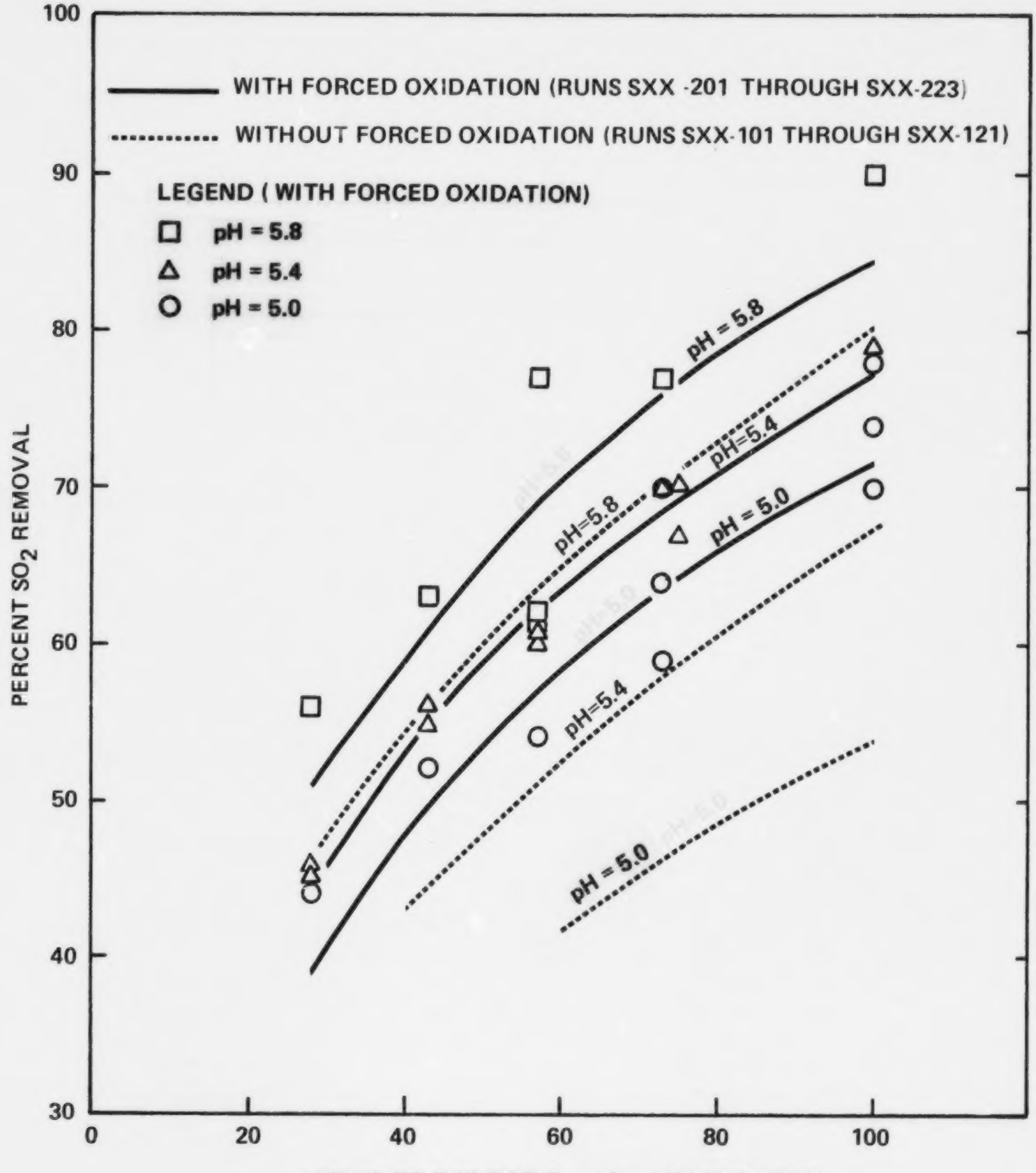


Figure 22-11

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal
With Two-Tank Forced Oxidation And Without Adipic Acid
(1600 gpm Maximum Slurry Rate)

22.5.3 Limestone Tests with Two-tank Forced-Oxidation at 2400 gpm Maximum Slurry Rate

Thirty-six limestone factorial runs, including 13 repeated runs, were made without adipic acid using two-tank forced oxidation. These tests were conducted after the spray tower system had been modified to give a maximum slurry flow capacity of 2400 gpm. The flow configuration is the same as that shown in Figure 12-1, except that adipic acid was not added to the effluent hold tank.

Table 22-8 gives the results of the 36 runs. Thirteen runs were repeated because of an inlet SO_2 analyzer problem. The operating conditions held constant during the runs were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Slurry solids concentration:	15 percent
Oxidation tank level:	18 ft (2.8 to 5.6 minutes residence time)
Effluent hold tank level:	8.5 ft (8.3 to 16.6 minutes residence time)
Air flow rate to oxidizer:	250 scfm
Solids dewatering equipment:	Clarifier and drum filter
Slurry flow rate:	600 gpm/header

The slurry flow rate per header was constant at 600 gpm. Three levels of slurry rate were tested at 1200, 1800, and 2400 gpm (2,3, and 4 headers). The header positions and number in each run are as indicated in Table 22-8. Each of the four headers (spaced 4 ft apart) had 12 Bete No. ST48FCN nozzles. The top three headers sprayed downward and the bottom header sprayed upward. Three levels of scrubber inlet pH at 5.0, 5.4, and 5.8 were tested.

Equation 22-12 for predicting SO_2 removal has been fitted to 20 run-averaged data points (Table 22-8). Thirteen original runs which were subsequently repeated because of an inlet SO_2 meter problem, and three runs (Runs SXX421, SXX422, and SXX423) which used 1200 gpm with the bottom two headers instead of the normal practice of using the top two headers, were excluded from the correlation.

Table 22-8

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS USING TWO TANKS WITH FORCED OXIDATION AT 2400 GPM MAXIMUM SLURRY RATE

RUN NO.	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Sulfite** Oxid. (%)	Replicate	Headers***
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.			
SXX401	20,000	2400	150	1.8	.14	5.05-5.27	5.15	4.45	2590	2160-2680	2440	79-85	82.1	99.2	A	All
SXX402	27,500	1200	54	2.5	.19	4.94-5.19	5.05	3.95	2720	1920-2000	1950	38-46	40.6	99.5	B	3,4
SXX403	27,500	2400	109	2.9	.21	4.90-5.06	4.95	4.25	2840	2120-2320	2230	68-74	71.0	100	C	All
SXX403(R)	27,500	2400	109	2.5	.18	4.88-5.00	4.95	4.25	2715	2800-2880	2830	79-80	79.4	100	C	All
SXX404	35,000	2400	85	3.8	.28	4.96-5.07	5.00	4.00	2665	2320-2360	2345	61-66	63.2	100	D	All
SXX404(R)	35,000	2400	85	3.4	.30	4.83-5.01	4.95	4.05	2785	2720-2760	2730	71-73	72.3	98.7	D	All
SXX405	20,000	1800	112	2.0	.15	4.98-5.14	5.05	4.20	2700	2400-2720	2485	78-82	79.8	99.5		2,3,4
SXX406	27,500	1200	54	2.4	.21	4.84-5.09	5.00	4.10	2840	2640-2760	2690	55-60	56.3	100	B	3,4
SXX407	20,000	2400	150	2.0	.16	4.84-5.10	5.00	4.10	2710	2640-2760	2690	83-88	85.9	100	A	All
SXX423	27,500	1200	54	2.1	.24	5.09-5.27	5.20	3.70	2720	2480-2600	2530	42-51	46.5	100		1,2
SXX408	20,000	1800	112	2.2	.14	5.47-5.50	5.50	5.25	2735	2720-2800	2755	87-89	88.0	100	E	2,3,4
SXX408(R)	20,000	1800	112	1.8	.15	5.40-5.46	5.45	4.85	2345	2720-2800	2765	82-85	83.8	100	E	2,3,4
SXX409	35,000	2400	85	3.8	.29	5.32-5.35	5.35	4.95	2900	2480-2540	2500	75-80	77.0	99.2	F	All
SXX409(R)	35,000	2400	85	3.2	.29	5.43-5.50	5.45	5.00	2735	2800-2880	2825	75-78	76.9	100	F	All
SXX410	27,500	1200	54	2.5	.21	5.40-5.52	5.45	5.15	2520	2040-2240	2115	51-57	53.8	100	G	3,4
SXX410(R)	27,500	1200	54	2.4	.20	5.40-5.45	5.45	4.90	2735	2480-2640	2600	68-71	68.1	100	G	3,4
SXX410(R)	27,500	1200	54	2.1	.21	5.35-5.45	5.40	4.50	2910	2680-2900	2795	59-69	63.2	100	G	3,4
SXX411	20,000	2400	150	2.1	.15	5.32-5.45	5.40	4.95	2555	2560-2720	2640	89-92	90.2	100	H	All
SXX411(R)	20,000	2400	150	1.7	.13	5.38-5.40	5.40	5.05	2900	2900-2960	2925	93-94	93.0	99.5	H	All
SXX411(R)	20,000	2400	150	1.8	.14	5.42-5.58	5.50	5.10	2780	2720-2800	2755	91-92	91.9	100	H	All
SXX412	20,000	1800	112	2.0	.14	5.34-5.36	5.35	4.95	2875	2400-2480	2425	84-86	85.2	100	E	2,3,4
SXX413	35,000	2400	85	3.5	.27	5.35-5.41	5.40	4.95	2875	2800-2960	2885	80-83	81.0	99.6	F	All
SXX422	27,500	1200	54	2.1	.23	5.32-5.60	5.45	4.30	2645	2080-2320	2165	39-50	46.1	100		1,2

Table 22-8 (continued)

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS USING TWO TANKS WITH FORCED OXIDATION AT 2400 GPM MAXIMUM SLURRY RATE

Run No	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Sulfite** Oxid. (%)	Replicate	Headers***
				Total*	M.E	Range	Ave.			Range	Ave.	Range	Ave.			
SXX414	27,500	1200	54	2.1	.21	5.87-5.91	5.90	4.75	2610	2640-3000	2830	62-65	60.5	100	I	3,4
SXX414(R)	27,500	1200	54	2.1	.19	5.78-5.85	5.80	5.50	2870	2800-2840	2810	73-75	73.9	99.5	I	3,4
SXX415	20,000	2400	150	1.9	.15	5.73-5.89	5.80	5.10	2480	2560-2760	2665	88-92	90.0	99	J	All
SXX416	35,000	2400	85	3.4	.28	5.79	5.80	5.05	2555	2360-2640	2510	71-77	74.6	99	K	All
SXX416(R)	35,000	2400	85	3.2	.30	5.67-5.80	5.75	5.30	2770	2680-2760	2710	81-82	81.6	100	K	All
SXX417	27,500	1200	54	2.5	.21	5.65-5.99	5.75	5.30	2565	2000-2440	2230	56-66	60.1	100	I	3,4
SXX418	20,000	1800	112	1.8	.18	5.75-5.86	5.75	5.35	2520	2580-2840	2710	79-84	82.8	100	L	2,3,4
SXX418(R)	20,000	1800	112	1.7	.15	3.83-5.98	5.90	5.30	2485	2760-2840	2790	90-93	91.7	100	L	2,3,4
SXX419	20,000	2400	150	1.7	.14	5.77-5.80	5.80	5.00	2630	2440-2560	2500	85-86	85.4	100	J	All
SXX419(R)	20,000	2400	150	2.2	.14	5.80-5.86	5.85	5.45	2630	2320-2400	2360	88-90	89.1	100	J	All
SXX420	27,500	2400	109	3.0	.20	5.76-5.85	5.80	4.90	2690	2240-2560	2415	79-84	81.5	99.5	M	All
SXX420(R)	27,500	2400	109	2.4	.20	5.68-5.83	5.75	5.30	2645	2880-2940	2905	84-86	85.4	100	M	All
SXX421	27,500	1200	54	2.0	.23	5.80-5.85	5.85	5.30	2840	2360-2560	2460	51-55	53.6	99		1,2

* ΔP Between taps in front of presaturator and after mist eliminator (M.E)

** All Runs with 250 SCFM air in the oxidizer

*** Top Header is number 4.

$$\text{Fraction SO}_2\text{ Removal} = 1\text{-exp}\left[-6.66\text{x}10^{-3}\ (L/G)^{0.77}\ \exp(0.37\text{pH})\right] \qquad (22\text{-}12)$$

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = spray tower inlet liquor pH

The ranges of operating variables covered by the 20 correlated runs are:

Liquid to gas ratio = 54-150 gal/mcf
pH = 4.95-5.90
Gas flow rate = 20,000-35,000 acfm at 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm per header)
Inlet SO_2 concentration = 2360-2925 ppm
Sulfite oxidation = 98.7-100 percent

Equation 22-12 explains 93 percent of the variation in the data for SO_2 removal with a standard error of estimate of 2.2 percent SO_2 removal. Figure 22-12 is a plot of SO_2 removal as a function of spray tower L/G with inlet pH as a parameter for Series SXX400. The curves on the figure represent the predictions of Equation 22-12.

Three runs (Runs SXX421, SXX422, and SXX423) which were made at 1200 gpm using the bottom two headers (excluded from the correlation) had significantly lower SO_2 removals than Equation 22-12 would predict:

Run No.	Actual SO_2 Removal, %	Predicted SO_2 Removal, %
SXX423	46.5	62.6
SXX422	46.1	66.0
SXX421	53.6	71.4

This is to be expected because of the lower slurry residence time in the scrubber for these runs by use of lower header positions.

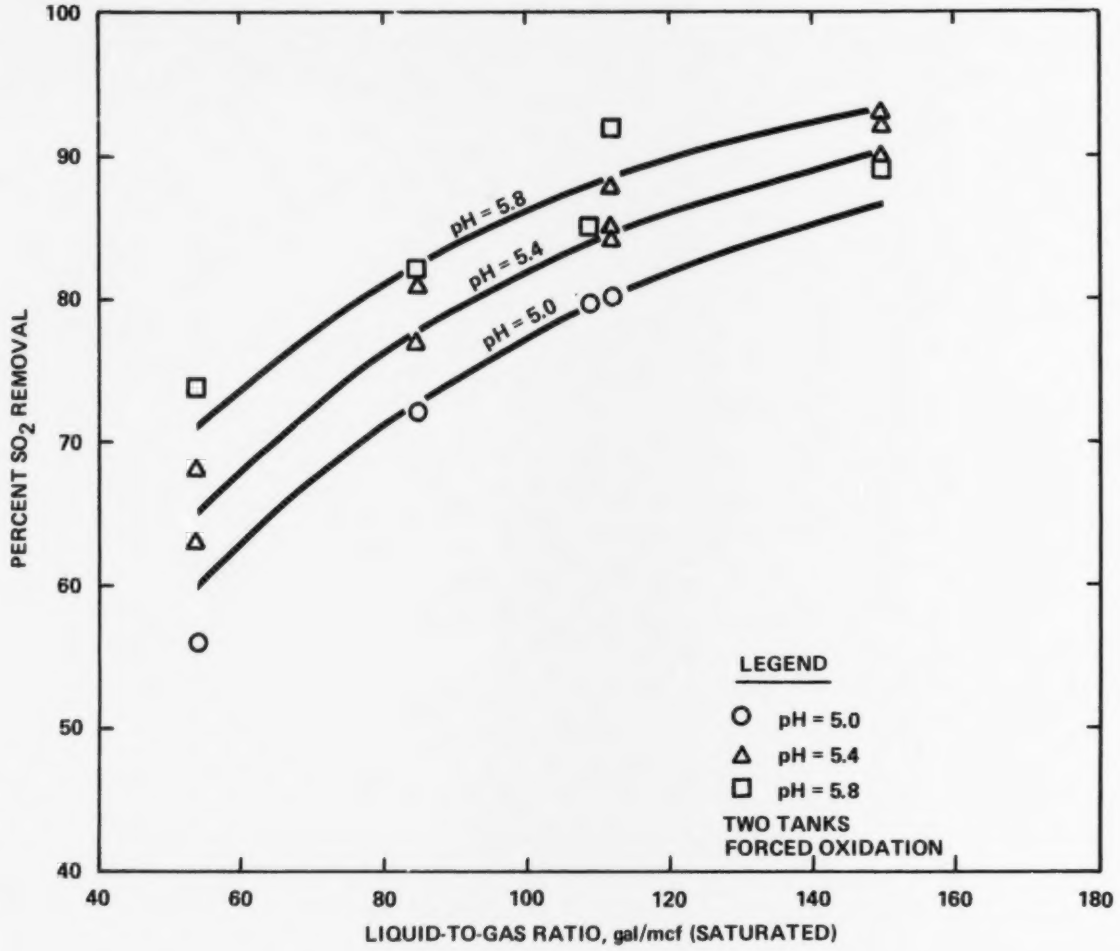


Figure 22-12

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal With Two-Tank Forced Oxidation And Without Adipic Acid (2400 gpm Maximum Slurry Rate)

22.5.4 Limestone Tests with One Tank without Forced-oxidation at 2400 gpm Maximum Slurry Rate

Twenty-three limestone tests, including three repeated runs, were made without adipic acid and without forced oxidation. These tests were conducted with up to 2400 gpm slurry rate. Figure 22-13 shows the flow configuration.

Table 22-9 presents the results of the 23 runs (Runs SXX301 through SXX320). The operating conditions common to all runs were:

Fly ash loading:	High (2 to 7 grains/dry scf)
Slurry solids concentration:	15 percent
Effluent hold tank level:	8.5 ft (8.3 to 16.6 minutes residence time)
Solids dewatering equipment:	Clarifier and drum filter
Slurry flow rate:	600 gpm/header

The design configuration of the four spray headers has been mentioned in Section 22.5.3. The number and positions of the headers used in each run are as indicated in Table 22-9.

Equation 22-13 for predicting SO_2 removal has been fitted to 23 run-averaged data points (Table 22-9).

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp\left[-1.48\times10^{-3}\,(L/G)^{0.68}\,\exp(0.69\text{pH})\right] \qquad (22\text{-}13)$$

The ranges of operating variables covered by the 23 correlated runs are:

Liquid-to-gas ratio = 54-150 gal/mcf
pH = 4.95-5.85
Gas flow rate = 20,000-35,000 acfm at 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm per header)
Inlet SO_2 concentration = 2605-2985 ppm
Sulfite oxidation = 23.3-41.5 percent

Equation 22-13 explains 91 percent of the variation in the data for SO_2 removal with a standard error of estimate of 3.4 percent SO_2 removal.

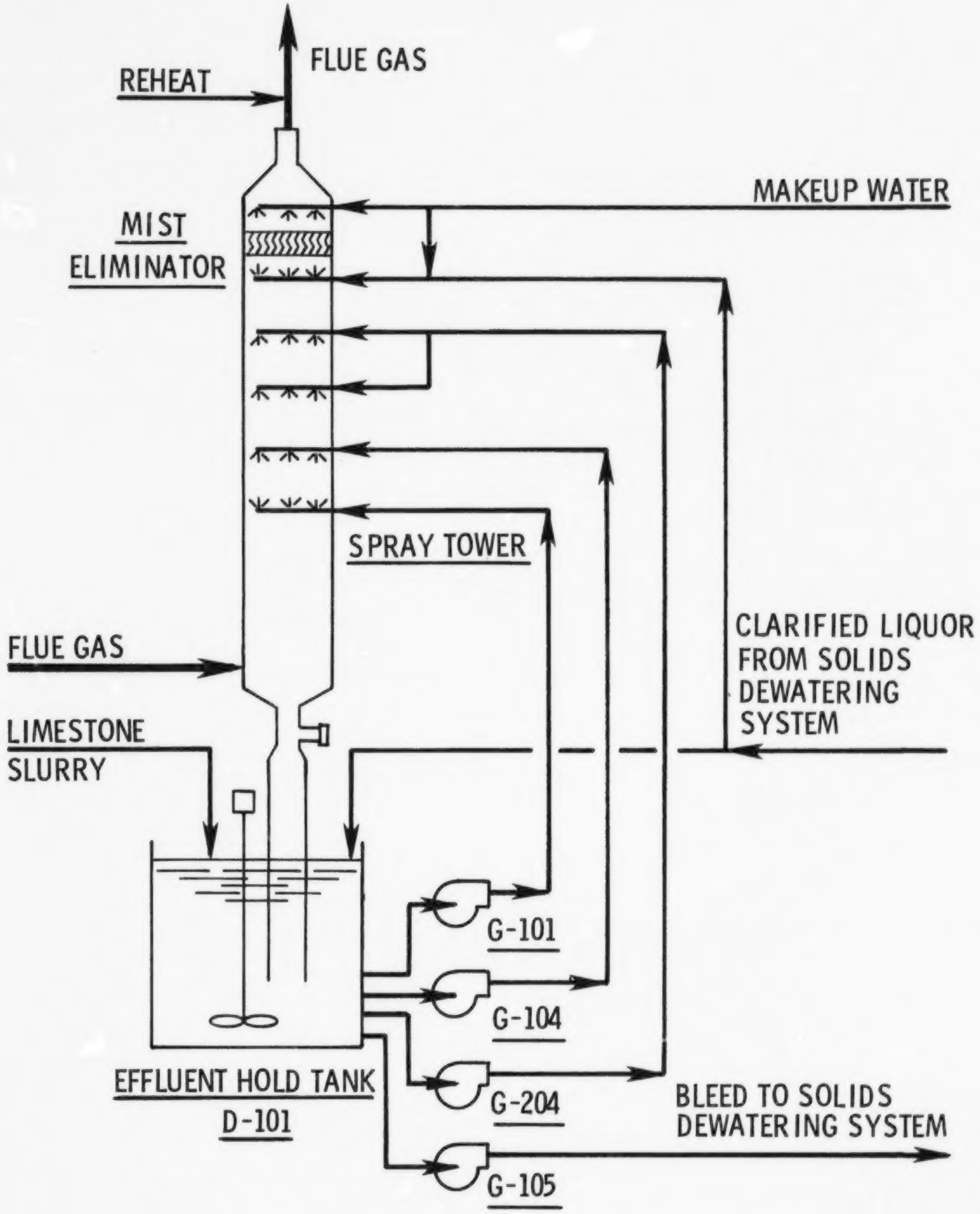

FLUE GAS
REHEAT
MAKEUP WATER
MIST ELIMINATOR
SPRAY TOWER
CLARIFIED LIQUOR FROM SOLIDS DEWATERING SYSTEM
FLUE GAS
LIMESTONE SLURRY
G-101
G-104
G-204
G-105
EFFLUENT HOLD TANK
D-101
BLEED TO SOLIDS DEWATERING SYSTEM

Figure 22-13

Spray Tower-Only Configuration Using A Single Tank Without Forced Oxidation (2400 gpm Maximum Slurry Flow Rate)

Table 22-9

RESULTS OF SPRAY TOWER LIMESTONE FACTORIAL TESTS WITH ONE TANK AND WITHOUT FORCED OXIDATION AT 2400 GPM MAXIMUM SLURRY RATE

Run No.	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Sulfite Oxid. (%)	Replicate	Headers**
				Total*	M.E	Range	Ave.			Range	Ave.	Range	Ave.			
SXX301	20,000	2,400	150	1.8	.14	4.87 - 5.14	4.95	4.75	2,485	2,560 - 2,680	2,630	70 - 78	73.7	31.0	A	All
SXX302	27,500	1,200	54	2.2	.21	4.95 - 5.03	5.00	4.60	2,590	2,920 - 3,000	2,960	53 - 59	56.2	33.6	B	3,4
SXX303	27,500	2,400	109	2.5	.22	4.86 - 5.04	4.95	4.65	2,750	2,820 - 3,000	2,945	62 - 72	65.7	34.5		All
SXX304	35,000	2,400	85	3.4	.33	4.95 - 5.21	5.10	4.70	2,810	2,760 - 3,000	2,880	54 - 65	58.5	36.1	G	All
SXX304(R)	35,000	2,400	85	3.5	.33	4.90 - 5.09	5.00	4.80	2,415	2,800 - 2,920	2,860	55 - 62	58.4	29.8	G	All
SXX305	20,000	1,800	112	1.8	.12	4.86 - 5.15	5.05	4.65	2,485	2,560 - 2,800	2,660	68 - 75	70.2	40.6		2,3,4
SXX306	27,500	1,200	54	2.2	.20	4.95 - 5.13	5.05	4.75	2,735	2,680 - 3,080	2,850	55 - 61	58.5	23.3	B	3,4
SXX307	20,000	2,400	150	1.7	.14	5.00 - 5.12	5.05	4.60	2,660	2,760 - 2,880	2,810	72 - 76	74.1	37.3	A	All
SXX308	20,000	1,800	112	1.8	.14	5.19 - 5.56	5.40	5.20	2,735	2,600 - 2,800	2,730	77 - 88	81.6	29.3	C	2,3,4
SXX309	35,000	2,400	85	3.4	.31	5.35 - 5.61	5.45	5.30	2,785	2,800 - 3,000	2,920	71 - 81	76.6	29.5	D	All
SXX310	27,500	1,200	54	2.2	.22	5.36 - 5.44	5.40	5.10	2,785	2,520 - 2,760	2,690	64 - 67	65.4	33.0		3,4
SXX311	20,000	2,300	143	1.7	.10	5.30 - 5.46	5.40	4.95	2,095	2,600 - 2,800	2,740	79 - 84	83.1	40.5		All
SXX312	20,000	1,700	106	1.7	.11	5.38 - 5.40	5.40	5.05	2,165	2,640 - 2,800	2,715	80 - 83	80.8	38.8	C	2,3,4
SXX313	35,000	2,300	82	3.3	.30	5.40 - 5.48	5.45	5.15	2,235	2,900 - 3,000	2,985	70 - 73	71.1	28.2	D	All
SXX313(R)	35,000	2,400	85	3.5	.31	5.40 - 5.43	5.40	4.85	2,465	2,760 - 2,880	2,810	68 - 70	68.7	40.0	D	All
SXX314	27,500	1,200	54	2.1	.24	5.71 - 5.78	5.75	5.35	2,270	2,520 - 2,720	2,605	64 - 67	65.5	29.5	E	3,4
SXX314(R)	27,500	1,200	54	2.1	.19	5.75 - 5.79	5.75	5.20	2,075	2,600 - 2,820	2,705	65 - 68	66.4	23.8	E	3,4
SXX315	20,000	2,300	143	1.8	.13	5.71 - 5.74	5.70	5.40	2,130	2,600 - 2,760	2,695	89 - 93	91.7	29.7	F	All
SXX316	35,000	2,300	82	3.4	.33	5.83 - 5.87	5.85	5.45	2,075	2,920 - 3,000	2,955	81 - 83	82.2	32.1		All
SXX317	27,500	1,200	54	2.0	.21	5.77 - 5.81	5.80	5.45	2,255	2,760 - 2,960	2,825	65 - 69	66.5	28.8	E	3,4
SXX318	20,000	1,800	112	1.8	.14	5.74 - 5.80	5.80	5.55	2,060	2,680 - 2,840	2,790	88 - 89	88.7	33.1		2,3,4
SXX319	20,000	2,400	150	1.8	.14	5.71 - 5.77	5.75	5.40	2,485	2,560 - 2,920	2,760	91 - 92	92.2	37.2	F	All
SXX320	27,500	2,400	109	2.5	.19	5.64 - 5.76	5.70	5.25	2,270	2,560 - 2,680	2,615	83 - 86	84.3	41.5		All

*△P between taps in front of presaturator and after mist eliminator (M.E.)

** Top header is number 4.

Figure 22-14 is a plot of SO_2 removal as a function of spray tower liquid-to-gas ratio with inlet pH as a parameter. The solid curves (from Equation 22-13) and the data points represent the tests without forced oxidation (Series SXX300). The dashed curves are obtained from Equation 22-12 for the test series with forced oxidation (Series SXX400) and are included in the figure for comparison.

As was the case with lower L/G operation (1600 gpm maximum slurry flow rate), the effect of forced oxidation on improved SO_2 removal was much greater for the lower pH runs. At the pH of 5.8 and L/G of 150 gal/mcf, the forced oxidation case showed an increase in SO_2 removal of 2.0 percentage points (from 91.3 to 93.3 percent), while at a pH of 5.0 and L/G of 150 gal/mcf, forced oxidation increased removal from 75.5 percent to 86.5 percent, an increase of 11.0 percentage points.

22.6 SPRAY TOWER-ONLY WITH LIMESTONE/ADIPIC ACID AND ONE-SCRUBBER-LOOP WITH AND WITHOUT FORCED OXIDATION

Two series of limestone factorial tests were conducted with adipic acid addition and with up to 2400 gpm maximum slurry flow rate in the spray tower (Series SAA100 and SAA200). These series were made from mid-October through mid-December 1980, and from mid-March through early-April 1981; these two periods were separated by the long-term spray tower limestone/adipic acid reliability run, Run 917-1A (see Section 12).

Series SAA100 was made with one tank without forced oxidation, whereas Series SAA200 was with two-tank forced oxidation. The two series were conducted to compare respectively with Series SXX300 and SXX400 (see Sections 22.5.4 and 22.5.3, respectively) in which no adipic acid was used.

In Series SAA200, a brief investigation was also made to observe the effects of number and position of spray headers on SO_2 removal.

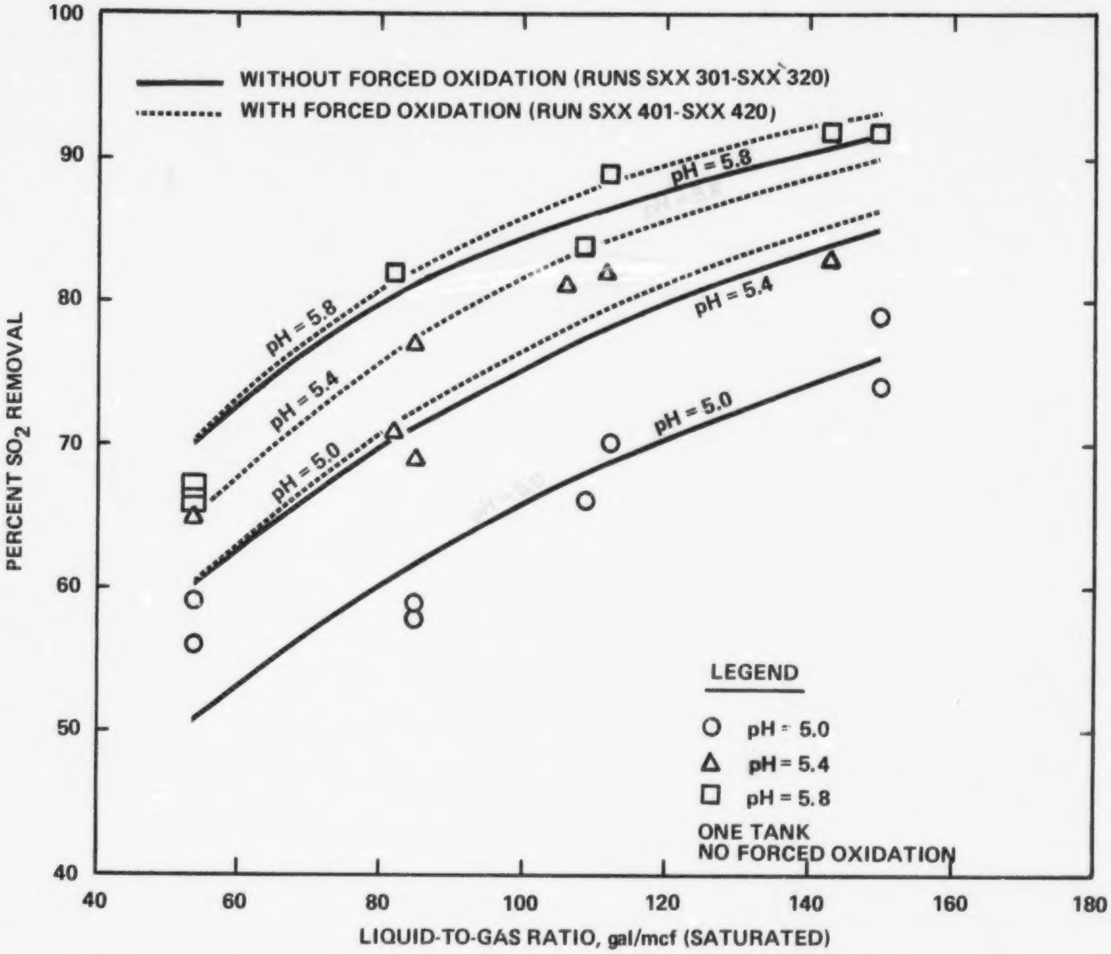


Figure 22-14

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal Without Forced Oxidation And Without Adipic Acid (2400 gpm Maximum Slurry Rate)

22.6.1 Limestone/Adipic Acid Tests with One Tank without Forced-Oxidation at 2400 gpm Maximum Slurry Rate

Twenty-eight runs, including two repeated tests (Runs SAA101 through SAA126), were conducted with adipic acid-enhanced limestone without forced oxidation. The flow configuration for these tests is the same as that shown in Figure 22-13 except that adipic acid was added to the effluent hold tank.

Table 22-10 summarizes the results of the 28 runs. Common operating conditions for these runs are the same as those listed for Series SXX300 in Section 22.5.4 Three nominal levels of adipic acid concentration of 900, 1300, and 2000 ppm were tested. Lower scrubber inlet pH levels of 4.6, 5.0 and 5.4 were used (compared to 5.0, 5.4, and 5.8 for Series SXX300).

Equation 22-14 for predicting SO_2 removal has been fitted to the 28 runs (Table 22-10):

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp\left[-4.5 \times 10^{-5} (L/G)^{0.86} \exp(1.2\ pH + 5.0 \times 10^{-4} A)\right] \quad (22\text{-}14)$$

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = scrubber inlet liquor pH
A = adipic acid concentration in scrubber liquor, ppm

The ranges of operating variables covered by the 28 correlated runs are:

L/G = 54-150 gal/mcf
pH = 4.50-5.50
A = 810-2300 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm/header)
Inlet SO_2 concentration = 2380-2995 ppm
Sulfite oxidation = 26.8-95.7 percent (natural oxidation)

Equation 22-14 explains 90 percent of the variation in the data for SO_2 removal with a standard error of estimate of 4.5 percent SO_2 removal.

Table 22-10

RESULTS OF SPRAY TOWER LIMESTONE/ADIPIC ACID FACTORIAL TESTS WITH ONE TANK AND WITHOUT FORCED OXIDATION AT 2400 GPM MAXIMUM SLURRY RATE

Run No.	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl$^-$ conc. (ppm)	Inlet SO_2 conc. (ppm)		Percent SO_2 Removal		Adipic Acid. conc (ppm)	Sulfite Oxid. (%)	Spray ** Headers	L.S. Stoich	Repli-cate
				Total*	M.E	Range	Ave.			Range	Ave.	Range	Ave.					
SAA101	27500	1200	54	2.8	0.19	5.01 - 5.06	5.05	4.80	2150	2520 - 2600	2550	54.7 - 59.0	57.0	860	35.8	3 & 4	1.07	
SAA102	27500	1200	54	2.2	0.19	5.31 - 5.48	5.40	5.00	1705	2340 - 2580	2460	64.2 - 70.2	67.8	970	26.8	3 & 4	1.08	
SAA103	35000	2400	85	3.5	0.34	4.83 - 5.07	4.95	4.70	2585	2120 - 2880	2525	54.9 - 66.7	60.9	810	40.8	All	1.04	A
SAA104	35000	2350	84	4.1	0.28	4.54 - 4.59	4.55	4.25	1975	2520 - 2600	2570	45.4 - 48.8	46.7	1030	61.6	All	1.04	
SAA105	35000	2350	84	3.9	0.30	4.93 - 5.06	5.00	4.75	1970	2240 - 2400	2380	69.3 - 72.7	70.9	860	43.3	All	1.05	A
SAA106	27500	2350	107	3.0	0.19	4.95 - 5.12	5.00	4.90	2135	2520 - 2600	2560	72.3 - 85.3	77.5	950	43.2	All	1.06	
SAA107	27500	2400	109	1.9	0.21	5.27 - 5.62	5.50	5.10	1910	2320 - 2660	2540	93.7 - 96.6	95.0	835	36.1	All	1.06	
SAA108	20000	2400	150	1.3	0.12	4.40 - 4.60	4.50	4.15	2235	2680 - 2920	2770	67.9 - 68.8	68.0	945	85.5	All	1.09	
SAA125	27500	2350	107	3.1	0.16	4.57 - 4.62	4.80	4.30	1970	2480 - 2680	2545	52.4 - 57.0	54.7	925	83.2	All	1.21	
SAA109	27500	1200	54	1.6	0.19	4.90 - 5.16	5.05	4.70	2370	2400 - 2880	2590	63.8 - 77.1	69.2	1220	35.2	3 & 4	1.06	B
SAA109(R)	27500	1200	54	1.7	0.18	4.80 - 5.05	4.95	4.55	1720	2640 - 2760	2690	71.4 - 73.1	71.7	1300	52.3	3 & 4	1.05	B
SAA110	27500	1200	54	1.7	0.20	5.30 - 5.50	5.40	4.95	2110	2640 - 2840	2745	78.9 - 84.0	81.3	1195	36.9	3 & 4	1.07	
SAA111	35000	2400	85	2.9	0.29	4.47 - 4.61	4.50	4.30	2075	2880 - 3040	2945	57.6 - 61.5	58.0	1135	84.2	All	1.55	C
SAA111(R)	35000	2400	85	3.0	0.28	4.49 - 4.50	4.50	4.25	1650	2600 - 2720	2665	64.4 - 66.4	65.4	1300	75.1	All	1.09	C
SAA112	35000	2400	85	3.0	0.29	4.97 - 5.10	5.00	4.75	2010	2700 - 2760	2735	73.9 - 85.3	78.2	1245	40.8	All	1.06	D
SAA113	35000	2400	85	3.0	0.30	5.33 - 5.50	5.45	4.90	2130	2600 - 2880	2725	93.7 - 95.7	95.2	1575	29.8	All	1.08	
SAA114	35000	2400	85	3.0	0.27	4.83 - 5.02	4.95	4.50	1685	2560 - 2680	2635	81.5 - 89.9	86.6	1325	62.8	All	1.04	D
SAA115	27500	2400	109	2.1	0.17	4.64 - 4.70	4.65	4.30	1915	2680 - 2800	2745	69.1 - 75.1	71.8	1230	80.5	All	1.03	
SAA116	27500	2400	109	2.0	0.16	4.86 - 5.10	4.95	4.75	1830	2520 - 2800	2655	84.3 - 95.7	88.0	1355	62.0	All	1.05	
SAA117	27500	1200	54	1.7	0.18	4.59 - 4.60	4.60	4.25	1740	2680 - 2800	2745	56.9 - 58.5	57.7	2020	69.6	3 & 4	1.20	
SAA118	27500	1200	54	1.6	0.18	5.04 - 5.07	5.05	4.35	2060	2640 - 2800	2700	76.8 - 77.6	77.2	2000	60.9	3 & 4	1.05	
SAA119	27500	1200	54	1.7	0.18	5.34 - 5.39	5.35	4.75	1650	2840 - 2920	2880	84.6 - 89.2	88.0	2000	56.8	3 & 4	1.09	
SAA120	35000	2400	85	3.1	0.29	4.93 - 5.08	5.00	4.70	1615	2760 - 2920	2860	86.7 - 92.8	89.8	2300	58.8	All	1.05	D
SAA121	35000	2400	85	3.1	0.30	4.50 - 4.54	4.50	4.20	1810	2700 - 2840	2760	62.7 - 67.4	65.2	1735	95.7	All	3.29	
SAA122	35000	2400	85	3.2	0.30	4.85 - 5.11	5.05	4.80	1450	2440 - 2840	2635	86.5 - 94.5	91.1	2130	60.0	All	1.08	D
SAA123	27500	2400	109	2.2	0.19	4.57 - 4.65	4.60	4.35	1455	2480 - 2960	2720	75.3 - 83.0	79.4	2010	59.1	All	1.11	
SAA124	27500	2400	109	2.2	0.20	4.91 - 5.04	5.00	4.65	1120	2920 - 3040	2995	90.4 - 94.9	92.5	1915	44.3	All	1.04	
SAA126	35000	2400	85	3.0	0.31	4.65 - 4.82	4.70	4.30	1530	2880 - 3000	2960	70.8 - 86.3	75.9	1975	62.2	All	1.06	

*ΔP between taps in front of presaturator and after mist eliminator (M.E.)
** Top Spray Header is number 4.

Figures 22-15 through 22-17 illustrate the effects of spray tower liquid-to-gas ratio and inlet liquor pH on SO_2 removal at adipic acid concentrations of 900, 1300, and 2000 ppm, respectively. The lines on the figures represent the predictions of Equation 22-14 with actual data points also shown.

It is logical to combine the correlation for Series SXX300 without adipic acid (Table 22-9 and Equation 22-13) with the present series of tests with adipic acid, both operated under the same system configuration (Figure 22-13). Equation 22-15 has been fitted to 51 spray tower runs, including 28 runs from Series SAA100 (Table 22-10) and 23 runs from Series SXX300 (Table 22-9), both series without forced oxidation:

$$\begin{array}{l}\text{Fraction } SO_2\\ \text{Removal}\end{array} = 1-\exp[-2.9 \times 10^{-4} \, (L/G)^{0.73} \exp(0.95 \text{ pH} + 4.0 \times 10^{-4} A)] \quad (22\text{-}15)$$

The ranges of variables covered by the 51 correlated runs are :

L/G = 54-150 gal/mcf
pH = 4.50-5.50 with adipic acid addition
      4.95-5.85 without adipic acid addition
A = 0-2300 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm/header)
Inlet SO_2 concentration = 2380-2995 ppm
Sulfite oxidation = 23.3-95.7 percent (natural oxidation)

Equation 22-15 explains 86 percent of the variation in the data for SO_2 removal with a standard error of estimate of 4.7 percent SO_2 removal.

22.6.2 Limestone/Adipic Acid Tests with Two-tank Forced-Oxidation at 2400 gpm Maximum Slurry Rate

Forty runs (Runs SAA201 through SAA239), including one repeated run, were made with adipic acid-enhanced limestone with two-tank forced oxidation. The flow configuration for these runs was the same as that shown in Figure 12-1.

Table 22-11 lists the results of the 40 runs. Operating conditions common to

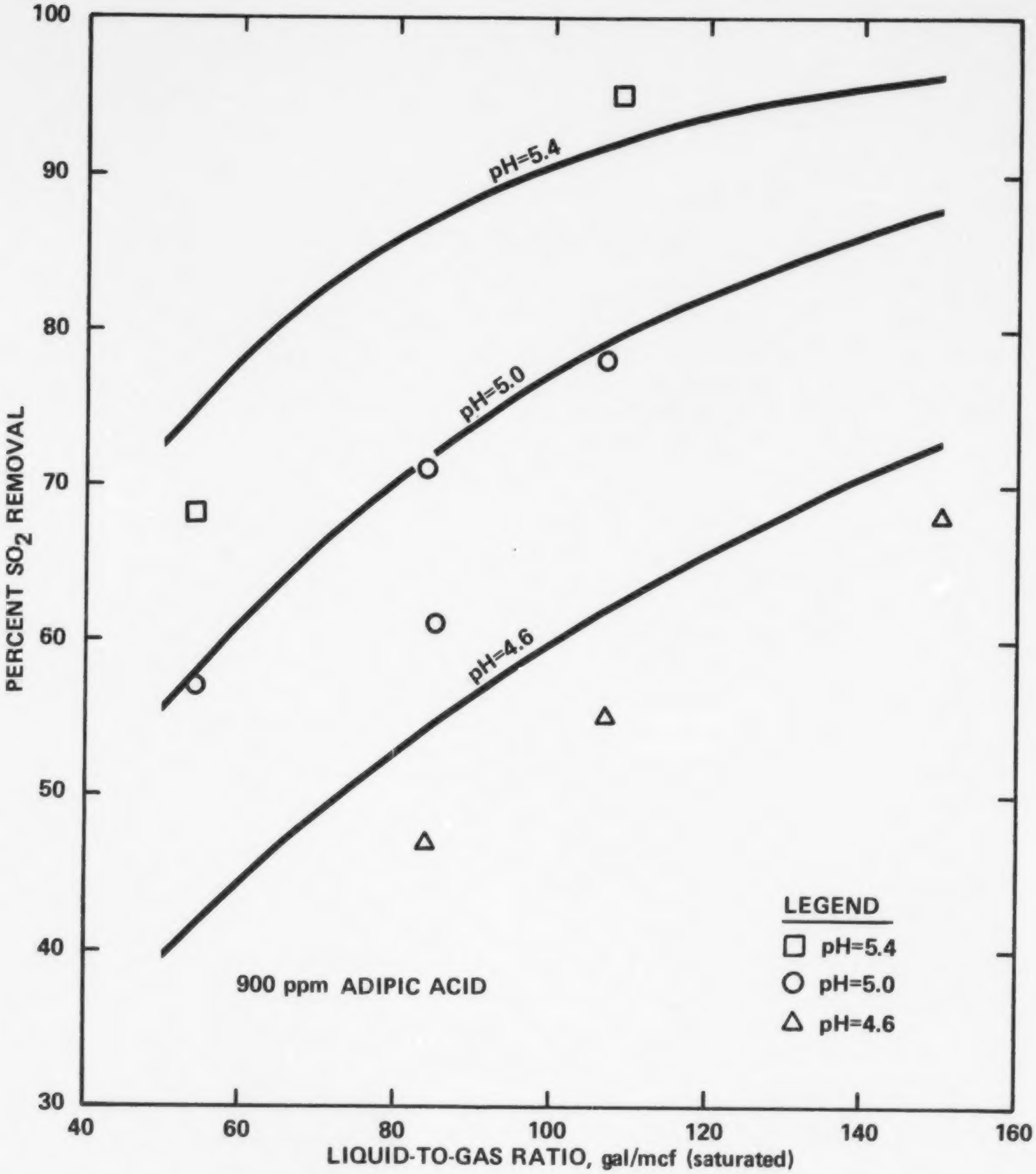


Figure 22-15

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal Without Forced Oxidation At 900 ppm Adipic Acid (2400 gpm Maximum Slurry Rate)

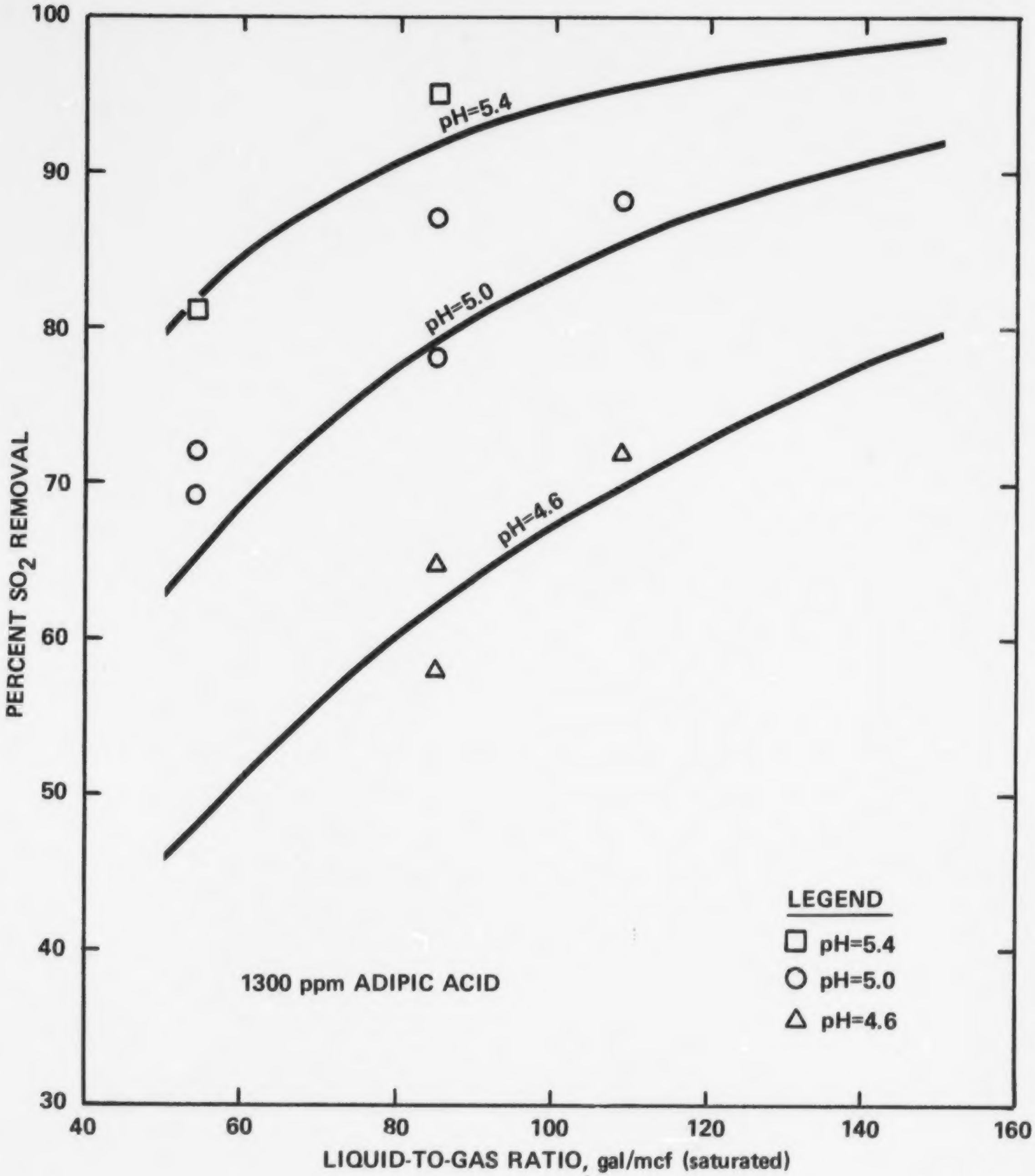


Figure 22-16

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal Without Forced Oxidation At 1300 ppm Adipic Acid (2400 gpm Maximum Slurry Rate)

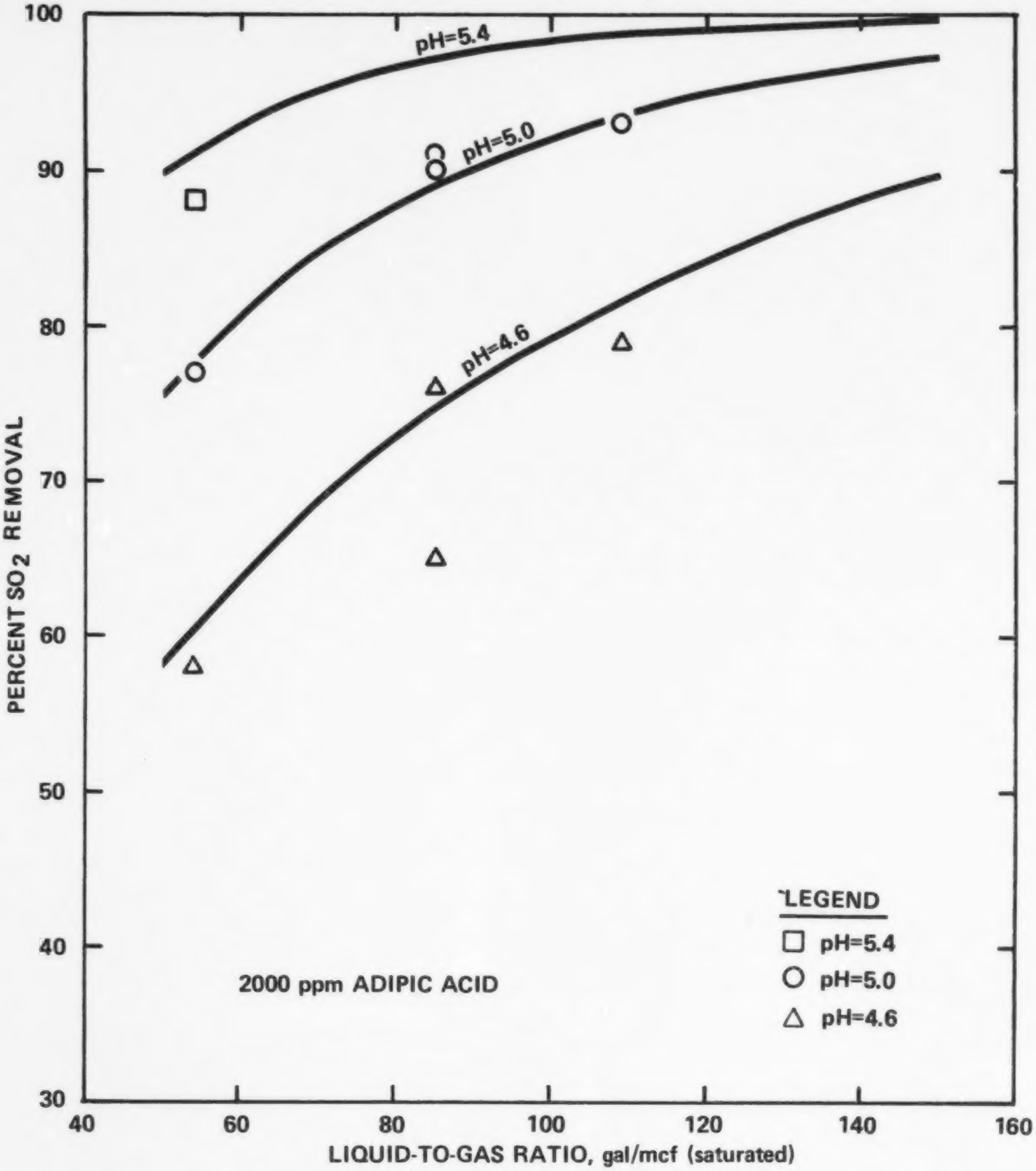


Figure 22-17

Effect Of Spray Tower L/G And Inlet pH On SO$_2$ Removal
Without Forced Oxidation At 2000 ppm Adipic Acid
(2400 gpm Maximum Slurry Rate)

Table 22-11

RESULTS OF SPRAY TOWER LIMESTONE/ADIPIC ACID FACTORIAL TESTS USING TWO TANKS WITH FORCED OXIDATION AT 2400 GPM MAXIMUM SLURRY RATE

RUN NO.	Gas Rate @300°F (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Ave. Cl^- conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Adipic Acid Conc. (ppm)	Sulfite Oxid. (%)	Spray** Headers	L.S. Stoich.	Replicates
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.					
SAA201	27,500	1200	54	1.9	0.12	4.95-5.15	5.05	4.65	1685	2840-3100	2930	68.1-69.6	69.2	860	100	3 & 4	1.06	
SAA202	27,500	1200	54	1.9	0.13	5.30-5.47	5.40	4.95	1660	2600-2680	2640	79.4-80.8	80.6	800	99.5	3 & 4	1.77	
SAA203	35,000	2400	85	2.6	0.26	4.95-4.99	4.95	4.35	1510	2800-3160	3050	87.5-90.5	88.2	835	100	ALL	1.03	A
SAA204	35,000	2400	85	2.6	0.23	4.52-4.61	4.60	3.45	1670	2640-2860	2750	77.6-80.7	79.6	970	100	ALL	1.01	
SAA205	35,000	2400	85	2.6	0.23	4.98-5.06	5.00	4.45	1710	2400-2840	2730	83.9-91.2	86.9	935	99.8	ALL	1.03	A
SAA206	27,500	2400	109	1.8	0.18	5.03-5.07	5.05	4.65	1660	2720-2880	2815	95.4-96.1	96.0	985	99.8	ALL	1.05	
SAA207	27,500	2400	109	2.2	0.14	5.44-5.47	5.45	5.10	1690	2640-2720	2670	93.9-95.0	94.2	860	100	ALL	2.46	
SAA208	20,000	2400	150	1.6	0.06	4.60-4.62	4.60	4.10	1840	2840-2920	2875	90.4-91.1	90.9	945	100	ALL	1.00	
SAA235	27,500	2400	109	2.3	0.12	4.50-4.70	4.65	3.65	1800	2800-2920	2870	80.3-82.9	81.4	910	100	ALL	1.03	
SAA236	20,000	2400	150	1.1	0.10	5.04-5.08	5.05	4.60	1560	2800-3040	2865	98.0	98.0	1125	99.2	ALL	1.02	
SAA237	35,000	2400	85	3.0	0.19	5.33-5.41	5.35	5.00	1600	2600-2800	2710	89.0-91.3	90.5	850	100	ALL	2.39	
SAA238	20,000	2400	150	1.5	0.08	5.29-5.37	5.35	5.05	1845	2720-2840	2785	96.8-98.0	97.4	820	99.5	ALL	1.33	
SAA239	27,500	1200	54	1.8	0.14	4.57-4.62	4.60	3.75	1980	2880-2920	2890	62.6-63.9	63.4	865	100	3,4	1.00	
SAA209	27,500	1200	54	1.6	0.15	4.90-4.94	4.90	4.20	1585	2240-3080	2800	80.4-83.2	81.5	1385	100	3,4	1.02	
SAA210	27,500	1200	54	1.6	0.15	5.29-5.43	5.35	5.25	1455	2920-3080	2955	86.7-87.9	87.5	1415	100	3,4	1.61	
SAA211	35,000	2400	85	3.0	0.21	4.47-4.73	4.65	3.65	1420	3000-3120	3090	85.2-92.6	88.6	1440	99.8	ALL	1.00	B
SAA212	35,000	2400	85	2.9	0.23	4.80-5.05	4.95	4.35	1525	2920-3080	2995	91.6-94.1	93.4	1315	100	ALL	1.05	C
SAA213	35,000	2400	85	2.8	0.23	5.33-5.44	5.40	5.20	1545	2640-2840	2730	95.8	95.8	1360	95.6	ALL	2.06	
SAA214	35,000	2400	85	2.9	0.25	4.93-5.00	4.95	4.50	1615	2800-2880	2835	92.2-93.4	92.9	1365	100	ALL	1.10	C
SAA215	27,500	2400	109	1.9	0.14	4.44-4.58	4.50	4.10	1710	2840-3160	3030	87.6-94.8	90.9	1195	99.6	ALL	1.02	
SAA216	27,500	2400	109	1.9	0.13	4.44-5.05	5.00	4.55	1545	2860-2960	2905	94.8-96.1	95.6	1325	99.6	ALL	1.14	D
SAA228	27,500	1200	54	1.5	0.14	4.58-4.84	4.65	3.55	1845	2500-2880	2670	75.8-78.7	76.8	1430	100	3,4	1.01	
SAA229	35,000	1800	64	2.6	0.25	4.95-4.97	4.95	4.45	1775	2800-3000	2865	86.7-87.7	87.3	1200	100	2,3,4	1.04	
SAA230	27,500	2400	109	2.0	0.14	5.38-5.41	5.40	4.85	1555	2440-2680	2600	96.0-97.5	97.0	1215	99.5	ALL	1.90	
SAA231	35,000	2400	85	2.8	0.25	4.57-4.63	4.60	3.65	1755	2720-2840	2810	89.9-92.1	90.7	1180	100	ALL	1.01	B
SAA232	20,000	2400	150	1.1	0.12	4.55	4.55	3.70	1685	2800-2880	2825	97.3	97.3	1240	100	ALL	1.01	
SAA233	20,000	2400	150	1.1	0.12	4.98-5.06	5.05	4.60	1740	2600-2880	2735	98.8	98.8	1210	100	ALL	1.02	
SAA234	27,500	2400	109	1.8	0.13	5.00-5.03	5.00	4.65	1930	2840-3080	2995	94.8-96.1	95.5	1275	100	ALL	1.03	D
SAA217	27,500	1200	54	1.6	0.14	4.61-4.75	4.65	4.45	1455	2520-2760	2660	79.0-83.3	79.8	2000	99.6	3,4	1.00	
SAA218	27,500	1200	54	1.6	0.14	5.04-5.17	5.10	4.30	1470	2680-2800	2720	86.9-88.6	87.5	2150	100	3,4	1.01	
SAA219	27,500	1200	54	1.6	0.15	5.37-5.44	5.40	4.85	1455	2800-3000	2865	86.7-89.1	88.3	2135	100	3,4	1.41	
SAA220	35,000	2400	85	2.7	0.23	5.08-5.12	5.10	4.65	1365	2280-2480	2380	97.6	97.6	1900	100	ALL	1.02	E
SAA221	35,000	2400	85	3.2	0.23	4.62-4.66	4.65	3.80	1440	2720-2820	2785	92.9-93.7	93.2	1775	100	ALL	1.00	
SAA221(R)	35,000	2400	85	2.8	0.25	4.49-4.65	4.60	4.45	1560	520-1000	660	95.8-98.9	98.2	2165	99.5	ALL	1.01	
SAA222	35,000	2100	75	2.7	0.26	5.02-5.06	5.05	4.50	1475	2820-3000	2935	92.6-95.5	94.3	2135	100	ALL	1.02	
SAA223	27,800	2100	94	1.9	0.20	4.50-4.74	4.65	3.90	1215	2760-2920	2845	90.7-96.9	94.0	2100	99.8	ALL	1.00	
SAA224	27,400	2100	96	1.6	0.20	4.89-4.98	4.95	4.30	1385	2880-2920	2910	93.6-96.2	95.4	1975	99.6	ALL	1.01	
SAA225	35,000	2400	85	2.9	0.25	4.93-5.01	4.95	-	1720	2560-2760	2635	95.8	95.8	2080	100	ALL	1.02	E
SAA226	27,500	2400	109	2.0	0.12	4.55-4.67	4.60	4.00	1420	2760-3000	2940	94.8-95.8	95.3	1960	99.6	ALL	1.01	
SAA227	27,500	2400	109	1.9	0.15	4.98-5.02	5.00	4.55	1560	2760-2880	2830	97.6	97.6	2220	100	ALL	1.03	

*ΔP Between taps in front of presaturator and after mist eliminator (M.E.)

** Top Spray header is Number 4

these runs are the same as those listed for Series SXX400 in Section 22.5.3. The adipic acid concentration was tested at three levels of 900, 1300, and 2000 ppm. Lower scrubber inlet pH levels of 4.6, 5.0, and 5.4 were used, compared to 5.0, 5.4, and 5.8 for Series SXX400.

Equation 22-16 for predicting SO_2 removal has been fitted to the 39 runs in Table 22-11. Run SAA221(R) was excluded from the correlation because of the low inlet SO_2 concentration.

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp[-2.5 \times 10^{-3} (L/G)^{0.92} \exp(0.47pH + 4.0 \times 10^{-4}A)] \quad (22\text{-}16)$$

The ranges of operating variables covered by the 39 correlated runs are:

L/G = 54-150 gal/mcf
pH = 4.50-5.45
A = 800-2220 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm/header)
Inlet SO_2 concentration = 2380-3090 ppm
Sulfite oxidation = 95.6-100 percent (forced oxidation)

Equation 22-16 explains 89.0 percent of the variation in the data for SO_2 removal with a standard error of estimate of 2.8 percent SO_2 removal.

Figures 22-18 through 22-20 illustrate the effects of spray tower liquid-to-gas ratio and inlet liquor pH on SO_2 removal at adipic acid concentrations of 900, 1300, and 2000 ppm, respectively. The lines on the figures represent the predictions of Equation 22-16 with actual data points also shown.

Since the present series of tests with adipic acid (Table 22-11 and Equation 22-16) and Series SXX400 without adipic acid (Table 22-8 and Equation 22-12) were operated under the same system configuration (Figure 12-1), it is logical to combine the two series of tests into a single correlation. Equation 22-17 has been fitted to 59 spray tower runs, including 39 runs from Series SAA200 (Table

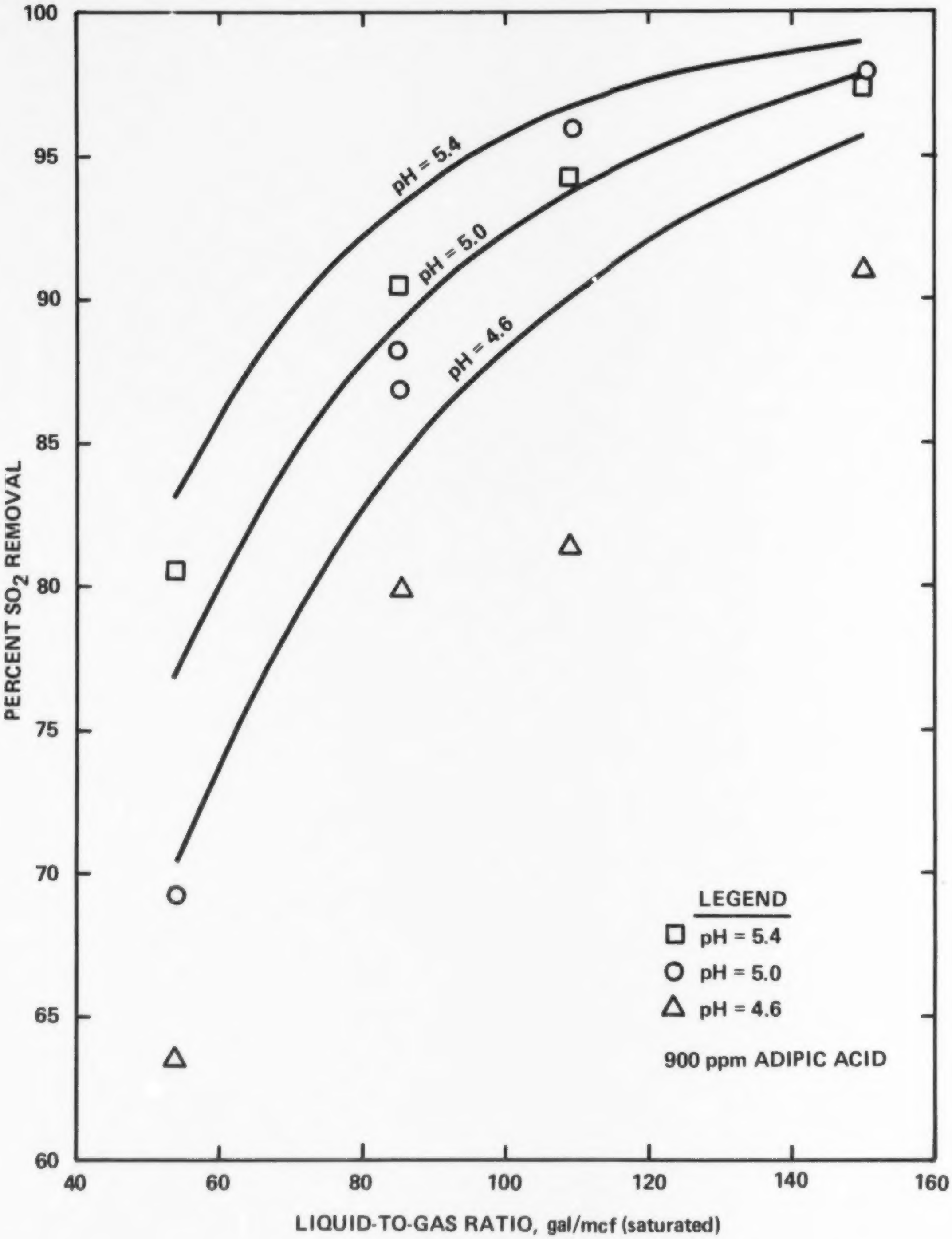


Figure 22-18

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal With Two-Tank Forced Oxidation At 900 ppm Adipic Acid (2400 gpm Maximum Slurry Rate)

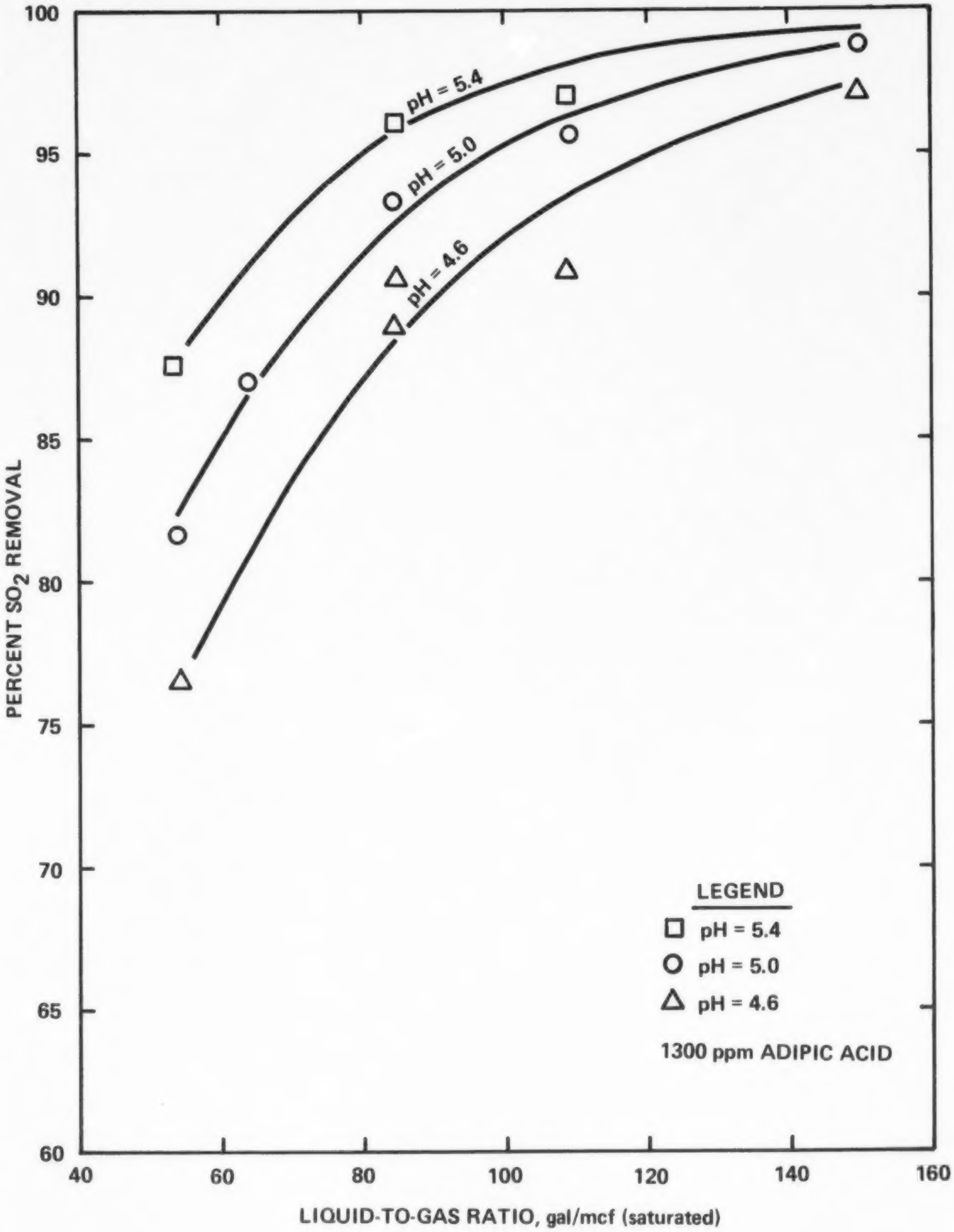


Figure 22-19

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal With Two-Tank Forced Oxidation At 1300 ppm Adipic Acid (2400 gpm Maximum Slurry Rate)

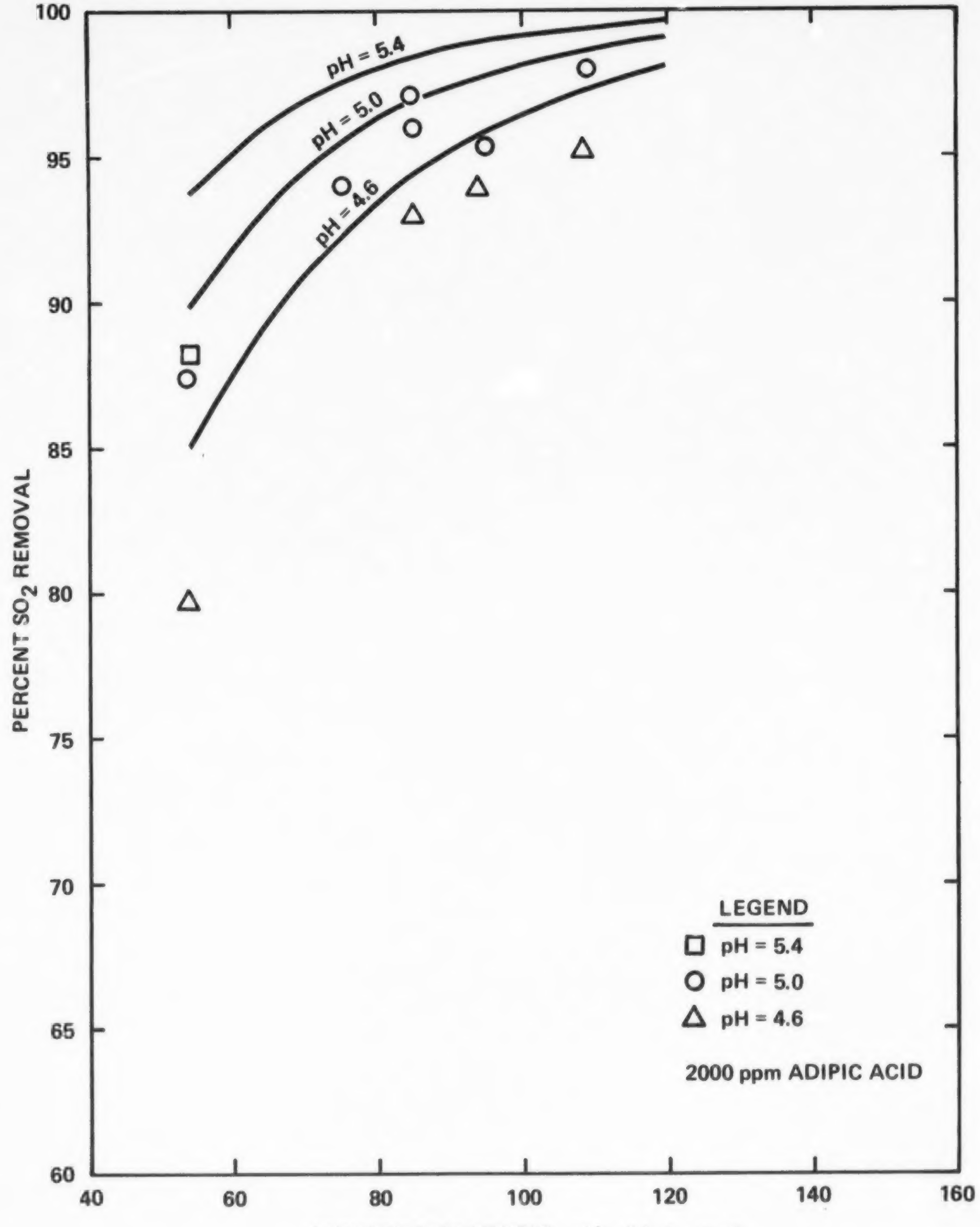


Figure 22-20

Effect Of Spray Tower L/G And Inlet pH On SO_2 Removal With Two-Tank Forced Oxidation At 2000 ppm Adipic Acid (2400 gpm Maximum Slurry Rate)

22-11) and 20 runs from Series SXX400(Table 22-8), both series wtih two-tank forced oxidation:

$$\text{Fraction } SO_2 \text{ Removal} = 1\text{-exp}\,[-4.3\text{x}10^{-3}(L/G)^{0.87}\text{exp}(0.37\text{pH}+4.0\text{x}10^{-4}A)] \qquad (22\text{-}17)$$

The ranges of variables covered by the 59 correlated runs are:

L/G = 54-150 gal/mcf
pH = 4.50-5.45 with adipic acid addition
= 4.95-5.90 without adipic acid addition
A = 0-2220 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 1200-2400 gpm (600 gpm/header)
Inlet SO_2 concentration = 2360-3090 ppm
Sulfite oxidation = 95.6-100 percent (forced oxidation)

Equation 22-17 explains 90.6 percent of the variation in the data for SO_2 removal with a standard error of estimate of 2.8 percent SO_2 removal.

As was the case without adipic acid addition (see Section 22.5, Figures 22-11 and 22-14), forced oxidation significantly improves SO_2 removal for tests with adipic acid, especially at low pH. Comparison of Figures 22-16 and 22-19, for example, shows that at 1300 ppm adipic acid, 5.4 scrubber inlet pH, and 85 gal/mcf liquid-to-gas ratio, SO_2 removal was 96 percent with forced oxidation compared to 92 percent without forced oxidation. At a lower scrubber inlet pH of 4.6, forced oxidation increased the removal from 62 to 88 percent, an increase of 26 percentage points.

22.6.3 Effect of Number and Position of Spray Headers on SO_2 Removal

Nineteen runs, including four repeated runs, were made to investigate the effect of various combinations of spray header position and number on SO_2 removal. Limestone slurry with 900 ppm adipic acid was used. Oxidation was forced in the first tank of two series tanks. The flow configuration is shown in Figure 12-1.

Table 22-12 gives the results of Runs SAA251 through SAA265. Common operating conditions were:

Fly ash loading: High (2-7 grains/dry scf)
Slurry solids concentration: 15 percent
Scrubber inlet pH: 5.0
Liquid-to-gas ratio: 64 gal/mcf
Adipic acid concentration: 900 ppm
Oxidation tank level: 18 ft (3.8-5.6 minutes residence time)
Effluent hold tank level: 8.5 ft (11.1-16.6 minutes residence time)
Air flow rate to oxidizer: 250 scfm
Solids dewatering equipment: Clarifier and drum filter

All headers sprayed slurry downward, except for Runs SAA264 and SAA265 in which the bottom header sprayed upward. The slurry flow rate was 600 gpm per header, except for Run SAA262 in which the flow rate was 1800 gpm using all four headers (450 gpm/header). The number and position of headers used in each run were as indicated in Table 22-12.

It should be noted that, in runs using less than four headers, the unused headers were not physically removed from the spray tower. Therefore, these unused headers presented an interference on the spray pattern of the slurry from headers above.

In general, higher SO_2 removal was obtained with higher header position, with all other conditions held constant. This would be expected because of the longer gas-slurry contact time offered by the higher header locations. For example, operating with Nos. 3 and 4 headers (Run SAA251, 80.2 percent SO_2 removal) was superior to operating with Nos. 1 and 4 (Run SAA253, 71.3 percent SO_2 removal).

Operating with the upper three headers (Run SAA258) gave higher SO_2 removal than operating with all four headers (Run SAA262) at the same 1800 gpm slurry rate (81.9 vs. 74.5 percent SO_2 removal). By having a higher flow rate per nozzle,

Table 22-12

RESULTS OF SPRAY TOWER LIMESTONE/ADIPIC ACID TESTS ON THE EFFECT OF SPRAY HEADER NUMBER AND POSITION

Run No.	Gas Rate @ 300°F (acfm)	Liquor Rate (gpm)	L/G gal/mcf)	Pressure Drop (inch H_2O)		S.T. Inlet Liquor pH		S.T. Outlet Liq. pH	Average Cl Conc. (ppm)	Inlet SO_2 Conc. (ppm)		Percent SO_2 Removal		Adipic Acid Conc. (ppm)	Sulfite Oxid. (%)	Spray** Headers	L.S. Stoich.	Replicates
				Total*	M.E.	Range	Ave.			Range	Ave.	Range	Ave.					
SAA251	23.4	1200	64	1.6	0.14	5.00-5.04	5.05	4.55	1970	2320-2440	2385	79.7-80.9	80.2	890	100	3,4	1.02	-
SAA252	23.4	1200	64	1.7	0.18	4.96-5.11	5.00	4.63	1935	2080	2080	76.0-77.0	76.5	935	100	2,4	1.05	A
SAA252(R)	23.4	1200	64	1.4	0.13	4.98-4.99	5.00	4.70	2075	2800-2960	2865	74.1-76.2	74.8	885	99.2	2,4	1.09	A
SAA233	23.4	1200	64	1.7	0.16	4.94-5.04	5.00	4.50	1830	2480-2600	2550	70.0-72.3	71.3	1000	100	1,4	1.34	D
SAA254	23.4	1200	64	1.4	0.15	5.00-5.10	5.05	4.40	1915	2280-2440	2330	71.8-75.9	74.1	920	100	2,3	1.02	-
SAA255	23.4	1200	64	1.5	0.14	4.95-4.97	4.95	4.24	1935	2200-2600	2305	68.0-74.2	71.5	925	100	1,3	1.00	C
SAA255(R)	23.4	1200	64	1.4	0.14	4.97-4.99	5.00	4.63	1955	2640-2920	2775	71.5-75.2	73.4	900	100	1,3	1.13	C
SAA256	23.4	1200	64	1.3	0.18	4.96-5.01	5.00	4.45	1990	2600-2800	2665	61.9-64.6	64.0	885	99.6	1,2	1.02	-
SAA257	23.4	1200	64	1.6	0.16	4.97-5.04	5.00	4.46	1845	2480-2510	2535	67.8-71.4	68.9	945	99.8	1,4	1.03	B
SAA257(R)	23.4	1200	64	1.5	0.11	5.01-5.04	5.00	4.63	1970	2800-2880	2845	73.4-75.0	74.2	940	100	1,4	1.19	B
SAA258	35.0	1800	64	3.1	0.27	4.99-5.14	5.05	4.63	1955	2320-2400	2370	81.5-82.0	81.9	900	100	2,3,4	1.03	-
SAA259	35.0	1800	64	3.0	0.24	5.03-5.06	5.05	4.54	2040	2300-2480	2425	76.5-80.2	78.9	970	100	1,3,4	1.03	D
SAA260	35.0	1800	64	3.3	0.32	4.96-5.02	5.00	4.59	1920	2280-2640	2530	69.2-73.2	71.0	930	100	1,2,4	1.11	-
SAA261	35.0	1800	64	2.8	0.28	4.95-5.01	5.00	4.42	1990	2160-2500	2300	70.9-75.3	72.9	980	99.6	1,2,3	1.02	E
SAA261(R)	35.0	1800	64	2.8	0.25	4.90-5.08	5.00	4.66	1760	2400-2680	2580	72.3-77.0	74.2	890	99.5	1,2,3	1.24	E
SAA262	35.0	1800	64	2.7	0.28	5.03-5.09	5.05	4.69	2015	2600-2680	2645	73.5-75.2	74.5	910	100	All	1.08	-
SAA263	35.0	1800	64	2.9	0.28	5.04-5.05	5.05	4.75	1970	2560-2600	2585	78.7-80.1	79.8	955	100	1,3,4	1.06	D
SAA264	35.0	1800	64	2.8	0.22	4.99-5.03	5.01	4.69	1630	2760-2840	2800	79.0-76.2	77.4	950	100	1,3,4(1)	1.14	-
SAA265	35.0	1800	64	2.7	0.26	4.99-5.09	5.05	4.65	1740	2680-2720	2700	72.7-76.7	74.9	910	99.1	1,2,4(1)	1.23	-

* Δ P between taps in front of presaturator and after mist eliminator (M.E)

** Top spray bank is Number 4. All spray headers spraying downward except noted

(1) Spray header No.1 (Bottom Header) spraying upward

the slurry breaks up into finer droplets at higher nozzle pressure drop, giving more surface area for mass transfer. Furthermore, operating with the top three headers should give higher gas-slurry contact time than operating with all four headers at the same total slurry flow.

Runs SAA264 and SAA265 show that by operating with the bottom spray header pointing upward, the SO_2 removal is slightly higher compared to the operation with the bottom header pointing downward (Runs SAA259 and SAA260).

22.7 SUMMARY OF SPRAY TOWER CORRELATIONS

A summary of the correlations given in Sections 22.5 and 22.6 is presented here for spray tower limestone tests with and without adipic acid, and with and without forced oxidation.

Table 22-13 summarizes the correlations for SO_2 removal in the spray tower into a general equation with the fitted coefficients listed separately for each case. The correlations explain an average of 91 percent of the variation in the data for SO_2 removal, and an average standard error of estimate of 3.3 percent SO_2 removal. The correlated data cover the following extreme ranges of the operating variables for the combined cases:

L/G = 14-150 gal/mcf
pH = 4.50-5.50 with adipic acid
   = 4.95-5.90 without adipic acid
A = 0-2300 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 400-2400 gpm
Inlet SO_2 concentration = 2000-3100 ppm
Sulfite oxidation = 95.6-100 with forced oxidation
                  = 10-95.7 without forced oxidation

Note that the above ranges of operating variables represent the extremes of all cases. Care must be exercised in determining the applicable ranges for the individual case by referring to Sections 22.5 and 22.6.

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L/G = 14-150 gal/mcf
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  = 4.95-5.90 without adipic acid
A = 0-2300 ppm
Gas flow rate = 20,000-35,000 acfm @ 300°F
Slurry flow rate = 400-2400 gpm
Inlet SO_2 concentration = 2000-3100 ppm
Sulfite oxidation = 95.6-100 with forced oxidation
  = 10-95.7 without forced oxidation

Note that the above ranges of operating variables represent the extremes of all cases. Care must be exercised in determining the applicable ranges for the individual case by referring to Sections 22.5 and 22.6.

TABLE 22-13

SUMMARY OF CORRELATIONS FOR SO_2 REMOVAL IN THE SPRAY TOWER WITH LIMESTONE SCRUBBING

$$\text{FRACTION } SO_2 \text{ REMOVAL} = 1-\exp\left[-\alpha_1(L/G)^{\alpha_2}\exp(\alpha_3 pH+\alpha_4 A)\right]$$

where:

L/G = spray tower liquid-to-gas ratio, gal/mcf
pH = scrubber inlet liquor pH
A = adipic acid concentration in scrubber liquor, ppm

TEST SERIES	SXX100	SXX200	SXX300	SXX400	SAA100	SAA200	SAA100 SXX300	SAA200 SXX400
Adipic acid addition	NO	NO	NO	NO	YES	YES	YES	YES
Forced oxidation	NO	YES	NO	YES	NO	YES	NO	YES
Number of tanks	1	2	1	2	1	2	1	2
Slurry rate/header, gpm*	400	400	600	600	600	600	600	600
α_1	4.4×10^{-4}	4.2×10^{-3}	1.48×10^{-3}	6.66×10^{-3}	4.5×10^{-5}	2.5×10^{-3}	2.9×10^{-4}	4.3×10^{-3}
α_2	0.71	0.73	0.68	0.77	0.86	0.92	0.73	0.87
α_3	0.84	0.47	0.69	0.37	1.2	0.47	0.95	0.37
α_4	0	0	0	0	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}
Number of runs	21	27	23	20	28	39	51	59
Percent variation explained	97	91	91	93	90	89	86	91
Std. error of estimate, %	2.5	3.4	3.4	2.2	4.5	2.8	4.7	2.8
Equation number	22-10	22-11	22-13	22-12	22-14	22-16	22-15	22-17
Table number	22-5	22-6	22-9	22-8	22-10	22-11	22-10 & 22-9	22-11 & 22-8

* The spray tower has 4 headers, spaced 4 ft apart. Bottom header sprays upward. Bete No. ST48FCN spray nozzles are used, with 7 nozzles/header for 400 gpm/header and 12 nozzles/header for 600 gpm/ header. Tower cross-sectional area is 50 ft^2.

22.8 TCA WITH LIMESTONE/ADIPIC ACID AND ONE-SCRUBBER-LOOP WITH AND WITHOUT FORCED OXIDATION

Sixty-four limestone/adipic acid partial factorial tests (Runs TAA001 through TAA064) were conducted on the TCA system in May, June, August, and October 1979 (see Figure 2-1). All but six of these runs were made with forced oxidation using two tanks. The flow configuration used for all the tests is shown in Figure 18-1. The detailed arrangement of the oxidation tank is shown in Figure 16-2. The external downcomer of the oxidation tank was used. Air to the oxidation tank was turned off for the six runs (Runs TAA013 through TAA016, TAA043, and TAA044) without forced oxidation.

Major variables investigated included adipic acid concentration, gas and slurry flow rates (liquid-to-gas ratio), total static bed height (zero or 15 inches of 1 7/8 inch diameter, 11.5 gram nitrile foam spheres), and scrubber inlet pH. The test results are listed in Table 22-14.

The 64 tests were divided into two groups:

- Testing at a controlled limestone stoichiometry of 1.2 moles Ca/mole SO_2 absorbed, giving a high scrubbber inlet pH of 5.6 to 6.1 (Runs TAA001 through TAA052).
- Testing at controlled lower scrubber inlet pH of 4.6 to 5.6 (Runs TAA053 through TAA064).

Operating conditions common to all tests were:

Fly ash loading:	High (2-7 grains/dry scf)
Slurry solids concentration:	15 percent
Oxidation tank level (7 ft diameter):	18 ft
Effluent hold tank level (20 ft diameter):	6.2 ft
Air flow to oxidizer:	220 scfm (for runs with forced oxidation)
Oxidation tank agitator speed:	54 rpm

Table 22-14

RESULTS OF TCA LIMESTONE/ADIPIC ACID FACTORIAL TESTS WITH ONE LOOP AND TWO TANKS

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Press. Drop (in. H_2O)	TCA Inlet Liquor pH		TCA Outlet Liq. pH	Ave. AD Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration, (ppm)		Percent SO_2 Removal		Air Rate (scfm)	Sulfite Oxid. (%)	Replicate	Spheres (inches)
					Range	Ave.				Range	Ave	Range	Ave.				
TAA001	25,000	898	44	6.3	5.66-5.76	5.71	5.0	648	1997	2000-2060	2014	89-91	89.9	220	100.0	A	15
TAA002	20,000	1184	73	5.9	5.61-5.74	5.66	5.1	651	2086	1860-2080	1919	96-97	96.4	220	99.6		15
TAA003	20,000	598	37	4.5	5.53-5.82	5.69	4.8	652	2130	1940-2320	2109	80-82	81.3	220	99.6		15
TAA004	30,000	904	37	7.5	5.65-5.67	5.66	4.8	618	2308	2120-2320	2219	88-91	89.4	220	99.6		15
TAA005	20,000	898	55	5.3	5.84-6.06	5.92	5.2	624	1864	2000-2300	2160	91-92	91.5	220	99.6		15
TAA006	25,000	906	45	6.4	5.66-5.88	5.80	4.8	635	1953	1960-2140	2171	90-92	90.8	220	100.0	A	15
TAA007	30,000	1186	49	8.9	5.67-5.75	5.72	5.0	595	2108	2120-2280	2169	93-95	93.9	220	99.5		15
TAA008	30,000	603	25	6.3	5.75-5.82	5.79	4.9	591	2485	2200-2440	2285	77-80	78.3	220	99.5		15
TAA009	25,000	1181	58	7.2	5.71-5.82	5.75	5.0	646	2418	2320-2520	2400	93-95	94.2	220	99.6		15
TAA010	25,000	597	29	2.0	5.97-6.02	6.00	5.0	644	2308	2400-2440	2420	59-61	59.5	220	99.1		0
TAA011	25,000	888	44	2.4	5.94-6.07	6.00	5.2	644	2374	2120-2200	2184	70-72	71.2	220	99.8		0
TAA012	25,000	1187	59	2.8	5.96-6.00	5.98	5.3	620	2352	2300-2400	2362	77-80	78.1	220	100.0		0
TAA013	25,000	1197	59	7.0	6.01-6.02	6.01	5.4	667	2219	2400-2440	2429	93-94	93.9	0	43.6	B	15
TAA014	25,000	590	29	5.2	6.11-6.14	6.12	5.2	529	1997	2600-2640	2631	77-80	78.4	0	36.5		15
TAA015	25,000	594	29	5.2	5.90-6.13	6.04	5.2	1389	1697	2320-2400	2340	87-88	87.8	0	30.3		15
TAA016	25,000	1176	58	7.0	5.89-6.07	5.97	5.3	1309	1598	2320-2520	2432	97-99	97.3	0	25.4	B	15
TAA017	25,000	894	44	2.3	5.93-6.26	6.05	5.3	1176	1790	2320-2780	2523	78-80	78.6	220	97.3	C	0
TAA018	25,000	587	29	2.1	6.07-6.23	6.13	5.1	1415	2130	2400-2460	2421	70-72	71.1	220	98.1		0
TAA019	25,000	1190	59	2.5	5.99-6.06	6.03	5.4	1423	2352	2440-2520	2474	86-87	86.2	220	99.1		0
TAA020	25,000	883	44	2.5	5.98-6.10	6.04	5.3	1316	2041	2680-2800	2750	78	78.0	220	99.6	C	0
TAA021	25,000	901	44	6.3	5.87-5.93	5.89	5.1	1273	2375	2280-2540	2398	92-94	93.5	220	99.3	D	15
TAA022	20,000	895	55	5.1	5.87-6.10	6.01	5.1	1144	1775	2720-2880	2804	93-95	94.0	220	99.9		15

Table 22-14 (continued)

RESULTS OF TCA LIMESTONE/ADIPIC ACID FACTORIAL TESTS WITH ONE LOOP AND TWO TANKS

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Press. Drop (in. H_2O)	TCA Inlet Liquor pH		TCA Outlet Liq. pH	Ave. $AD^=$ Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration, (ppm)		Percent SO_2 Removal		Air Rate (scfm)	Sulfite Oxid. (%)	Replicate	Spheres (inches)
					Range	Ave.				Range	Ave.	Range	Ave.				
TAA023	30,000	898	37	7.4	5.79-5.85	5.82	5.0	1384	1909	2460-2600	2546	93-94	93.9	220	99.8		15
TAA024	25,000	580	29	5.1	5.92-6.01	5.95	5.0	1287	1997	2600-2800	2651	84-86	85.6	220	99.7	E	15
TAA025	25,000	885	44	6.1	5.92-6.04	5.97	5.0	1287	2086	2160-2560	2378	94-96	95.2	220	99.5	D	15
TAA026	25,000	1192	59	7.1	5.82-5.91	5.87	5.2	1335	2041	1840-2080	1942	97-98	97.3	220	99.8		15
TAA027	25,000	604	29	5.5	5.87-6.01	5.94	5.0	1247	1930	2400-2680	2461	85-87	86.3	220	99.2	E	15
TAA028	25,000	893	44	6.1	5.76-5.89	5.85	5.1	2122	1331	2340-2720	2524	96-97	96.2	220	99.7	F	15
TAA029	25,000	601	29	5.2	5.97-6.06	6.01	5.0	1911	1287	2360-2400	2373	90-91	90.6	220	99.6	G	15
TAA030	30,000	905	37	7.6	5.49-5.64	5.56	5.0	1945	1598	2740-2960	2861	93-95	93.9	220	99.6		15
TAA031	20,000	901	55	5.0	5.86-5.91	5.88	5.1	2088	1442	2440-2480	2454	97-98	97.2	220	99.8		15
TAA032	25,000	900	44	6.1	5.79-5.82	5.80	5.1	1878	1775	2320-2520	2484	95-96	95.4	220	100.0	F	15
TAA033	25,000	1191	59	7.1	5.73-5.85	5.79	5.2	2116	1753	2360-2520	2443	97-98	97.9	220	99.9		15
TAA034	25,000	589	29	5.2	5.79-5.86	5.82	5.0	1916	1686	2280-2360	2329	90-91	90.4	220	100.0	G	15
TAA035	25,000	1203	59	2.7	5.64-5.90	5.76	5.2	2065	1775	2160-2540	2389	86-89	88.1	220	100.0		0
TAA036	30,000	895	37	3.3	5.63-5.79	5.71	5.0	2174	1819	2400-2440	2417	82-87	83.9	220	99.2		0
TAA037	30,000	602	25	2.6	5.69-5.83	5.77	4.9	2099	1953	2300-2520	2404	72-75	72.7	220	99.5		0
TAA038	20,000	898	55	1.8	5.64-5.75	5.70	5.0	2254	1775	2320-2560	2407	86-88	86.4	220	99.7	H	0
TAA039	20,000	596	37	1.4	5.70-5.77	5.74	4.9	2025	1864	2480-2600	2540	77-78	77.4	220	100.0		0
TAA040	30,000	1191	49	3.6	5.62-5.72	5.68	5.1	2245	1864	2240-2400	2287	87-88	87.2	220	99.4		0
TAA041	20,000	896	55	1.7	5.73-5.76	5.75	5.0	1981	1775	2560-2680	2625	83-86	83.8	220	99.2	H	0
TAA042	25,000	903	44	2.3	5.60-5.75	5.68	5.0	2284	1886	2320-2720	2487	80-85	81.8	220	99.7		0
TAA043	25,000	597	29	5.3	5.90-5.97	5.94	5.2	1955	1893	2320-2640	2472	89-92	90.3	0	30.4		15
TAA044	25,000	1191	59	7.1	5.85-5.90	5.88	5.3	2128	1953	2240-2280	2253	97-98	97.9	0	33.7		15(1)

(1) Actual measured sphere depth at the end of TAA-044 was 12-1/2 inches.

Table 22-14 (continued)

RESULTS OF TCA LIMESTONE/ADIPIC ACID FACTORIAL TESTS WITH ONE LOOP AND TWO TANKS

Run No.	Gas Rate (acfm)	Liquor Rate (gpm)	L/G (gal/mcf)	Press. Drop (in. H_2O)	TCA Inlet Liquor pH		TCA Outlet Liq. pH	Ave. $AD^=$ Conc. (ppm)	Ave. Cl^- Conc. (ppm)	Inlet SO_2 Concentration, (ppm)		Percent SO_2 Removal		Air Rate (scfm)	Sulfite Oxid. (%)	Replicate	Spheres (inches)
					Range	Ave.				Range	Ave.	Range	Ave.				
TAA045	25,000	900	44	2.3	5.94-6.20	6.08	5.2	0	3432	2400-2560	2452	53-58	55.4	220	99.8	I	0
TAA046	25,000	1193	60	2.7	5.79-5.89	5.82	5.1	0	3586	2080-2360	2208	65-66	65.1	220	97.7		0
TAA047	25,000	592	30	1.7	6.04-6.10	6.07	5.2	0	3515	1680-1740	1769	46-48	47.1	220	99.4		0
TAA048	25,000	887	44	2.3	6.18	6.18	5.3	0	3248	2000-2200	2094	57-59	57.9	220	99.6	I	0
TAA049	25,000	902	44	6.4	5.92-6.27	6.06	5.3	0	2568	2200-2280	2262	71-76	73.7	220	99.5	J	15
TAA050	25,000	1178	59	7.5	6.05-6.13	6.09	5.0	0	3248	2080-2160	2110	83-84	83.6	220	99.5		15
TAA051	25,000	575	29	5.1	5.88-5.97	5.92	5.0	0	3728	2000-2100	2071	56-59	57.5	220	99.5		15
TAA052	25,000	904	44	6.5	5.81-6.05	5.96	5.0	0	3269	2320-2520	2429	73-76	74.9	220	99.0	J	15
TAA053	25,000	905	44	6.6	5.51-5.82	5.62	5.2	707	2101	2000-2400	2191	84-90	86.6	220	96.3		15
TAA054	25,000	906	44	6.6	5.07-5.16	5.11	4.7	761	4112	2120-2600	2452	64-83	72.1	220	98.7		15
TAA055	25,000	907	44	6.7	4.47-4.63	4.57	3.6	667	3550	2240-2360	2331	44-50	46.9	220	99.4		15
TAA056	25,000	906	44	6.7	5.22-5.41	5.29	4.7	1247	3432	2240-2440	2329	88-92	90.5	220	100.0		15
TAA057	25,000	905	44	6.6	5.45-5.52	5.50	5.0	1249	2870	2240-2520	2365	88-92	89.7	220	100.0		15
TAA058	25,000	904	44	6.5	5.10-5.41	5.25	4.6	1409	2958	2200-2480	2272	86-89	87.4	220	99.6	K	15
TAA059	25,000	898	44	6.8	4.91-5.09	5.01	4.2	1273	2973	2000-2880	2246	68-84	76.0	220	99.5		15
TAA060	25,000	900	44	6.9	4.43-4.67	4.52	3.6	1333	2556	2520-2960	2800	54-64	62.9	220	100.0		15
TAA061	25,000	905	44	6.9	5.06-5.32	5.23	4.7	1497	2645	2500-2640	2528	89-92	91.0	220	98.6	K	15
TAA062	25,000	903	44	6.5	5.21-5.45	5.37	4.9	2102	2944	2200-2280	2263	94-95	95.0	220	99.5		15
TAA063	25,000	899	44	6.5	4.95-5.13	5.03	4.6	2088	2781	1640-1920	1776	92-94	93.7	220	99.6		15
TAA064	25,000	901	44	6.7	4.46-4.60	4.57	3.9	2109	2603	1600-1760	1690	82-85	83.8	220	100.0		15

22.8.1 Limestone/Adipic Acid Tests at High pH

Equation 22-18 for the prediction of SO_2 removal was fitted to the 52 TCA limestone/adipic acid factorial tests (Runs TAA001 through TAA052) made at a controlled limestone stoichiometry of 1.2 moles Ca/mole SO_2 absorbed. All but six of these runs were with forced oxidation. Eight runs (Runs TAA045 through TAA052) were base case runs without adipic acid additive.

$$\text{Fraction } SO_2 \text{ Removal} = 1-\exp[-0.0645\ L^{0.76}\exp(0.038h_s + 0.0177A^{0.5})] \quad (22\text{-}18)$$

where:

L = slurry flow rate, gpm/ft^2
h_s = total static height of 1-7/8 inch diameter, 11.5-gram nitrile foam spheres, inches
A = adipic acid concentration in scrubber liquor, ppm

The ranges of operating variables covered by Runs TAA001 through TAA052, and therefore by Equation 22-18, were:

Slurry flow rate (L) = 19-37 gpm/ft^2 (600-1200 gpm)
Gas flow rate = 20,000-30,000 acfm @ 300°F
Total height of spheres (h_s) = 0 or 15 inches
Number of grids = 4
Adipic acid concentration in scrubber liquor (A) = 0-2300 ppm
Scrubber inlet pH = 5.6-6.1 (1.2 limestone stoichiometry)
Inlet gas SO_2 concentration = 1800-2800 ppm
Sulfite oxidation = 97.3-100 percent for forced oxidation runs, and 25-44 percent for runs without forced oxidation

Equation 22-18 explains 98 percent of the variation in the data for SO_2 removal with a standard error of estimate of 1.8 percent SO_2 removal.

Figure 22-21 shows SO_2 removal as a function of adipic acid concentration and slurry flow rate for the TCA without spheres (grid tower). The lines in Figure 22-21 are predicted by Equation 22-18; the actual data points for no spheres are also shown in the figure. Figure 22-21 indicates

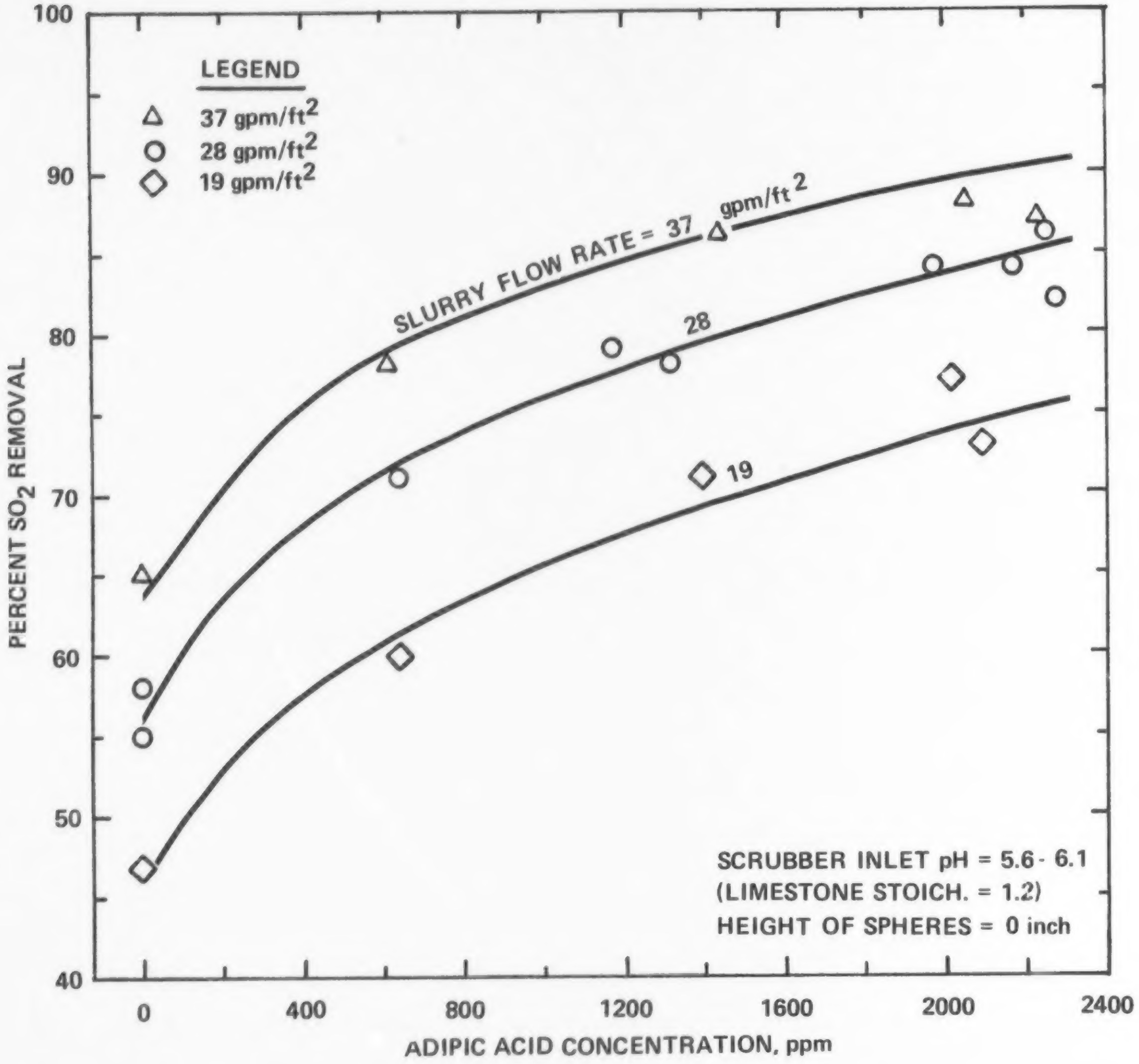

Figure 22-21. Effect of Adipic Acid Concentration And Slurry Flow Rate On SO_2 Removal In The TCA With Four Grids And Without Spheres (With Or Without Forced Oxidation)

that, for a slurry flow rate of 28 gpm/ft^2 (900 gpm for the Shawnee TCA), an increase in adipic acid concentration from zero to 1200 ppm increases SO_2 removal from 55 to 78 percent. Further increase of adipic acid concentration to 2000 ppm increases SO_2 removal to 85 percent. At an adipic acid concentration of 1200 ppm, an increase in slurry flow rate from 19 to 37 gpm/ft^2 increases SO_2 removal from 67 to 85 percent. Thus, for the grid tower configuration, either a doubling of the slurry flow rate or the addition of 1200 ppm of adipic acid cuts SO_2 emission by a factor of about two.

Figure 22-22 is a plot of SO_2 removal as a function of adipic acid concentration and slurry flow rate for the TCA with 15 inches of total static sphere height. Again, the lines in Figure 22-22 are predicted by Equation 22-18. For a slurry flow rate of 19 gpm/ft^2, adipic acid concentrations of zero, 600, and 2000 ppm gave SO_2 removal of 60-65, 80, and 90 percent respectively. For an adipic acid concentration of 600 ppm, doubling the slurry flow rate from 19 to 37 gpm/ft^2 increases SO_2 removal from 80 to 94 percent.

The effect on SO_2 removal of adding 15 inches of spheres is illustrated by comparing Figures 22-21 and 22-22. At a slurry flow rate of 37 gpm/ft^2 and zero adipic acid concentration, the addition of spheres increases SO_2 removal from 63 to 83 percent, corresponding to a decrease in SO_2 emmision by a factor of two. At a slurry flow rate of 19 gpm/ft^2 with 2000 ppm adipic acid, 15 inches of spheres increase SO_2 removal from 74 to 90 percent.

Note that Equation 22-18 applies both with and without forced oxidation. The effect of forced oxidation on the SO_2 removal was not statistically significant at the high scrubber inlet pH of 5.6 to 6.1 (1.2 limestone stoichiometry).

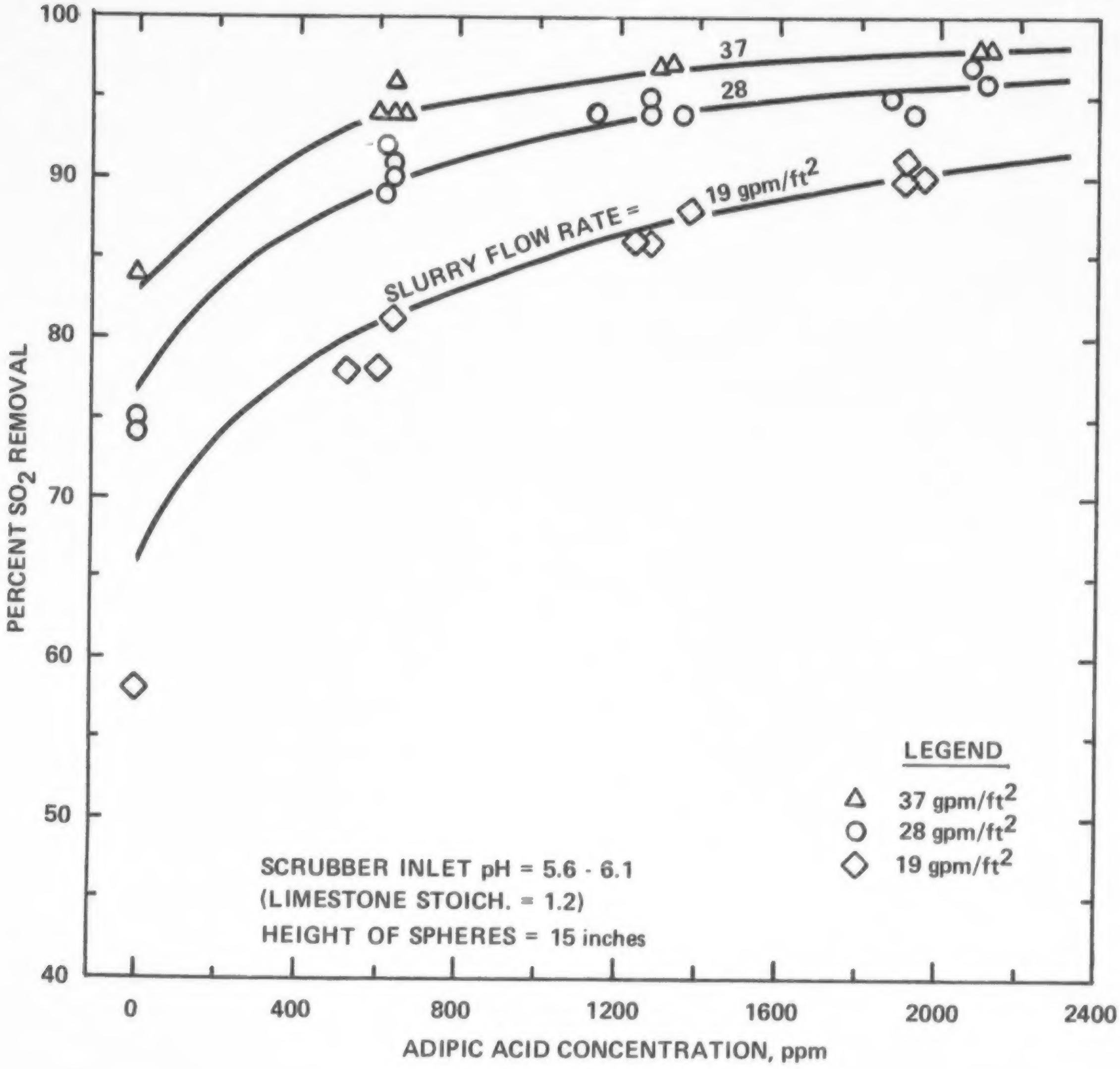

Figure 22-22. Effect Of Adipic Acid Concentation And Slurry Flow Rate On SO_2 Removal In The TCA With Four Grids And 15 Inches Of Spheres (With Or Without Forced Oxidation)

22.8.2 Limestone/Adipic Acid Tests at Low pH

Runs TAA053 through TAA064 were made to determine the effect of low, controlled scrubber inlet pH on SO_2 removal. All 12 runs were made with forced oxidation. The previous adipic acid runs with limestone stoichiometry controlled at 1.2 moles Ca/mole SO_2 absorbed, Runs TAA001 through TAA044, had demonstrated that pH had negligible effect on SO_2 removal at a constant limestone stoichiometry and a high scrubber inlet pH of 5.6 to 6.1.

Runs TAA053 through TAA064 include data for four levels of scrubber inlet pH: 4.6, 5.0, 5.3, and 5.6. The 5.6 pH level corresponded to a limestone stoichiometry of 1.2, and was thus a base case for comparison with the high pH tests. The adipic acid concentrations tested were 600, 1300, and 2000 ppm. The slurry and gas flow rates were constant at 900 gpm ($L = 28$ gpm/ft^2) and 25,000 acfm (at 300°F), respectively, and the total static height of spheres was 15 inches.

Equation 22-19 has been fitted to the SO_2 removal data for Runs TAA053 through TAA064:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp[-4.7 \times 10^{-3} \exp(\text{pH} + 6.2 \times 10^{-4} A)] \qquad (22\text{-}19)$$

where:

pH is that of the TCA inlet liquor, and A is the adipic acid concentration in ppm.

Equation 22-19 explains 98 percent of the variation in the SO_2 removal data, with a standard error of estimate of 2.2 percent SO_2 removal.

Figure 22-23 shows SO_2 removal as a function of adipic acid concentration

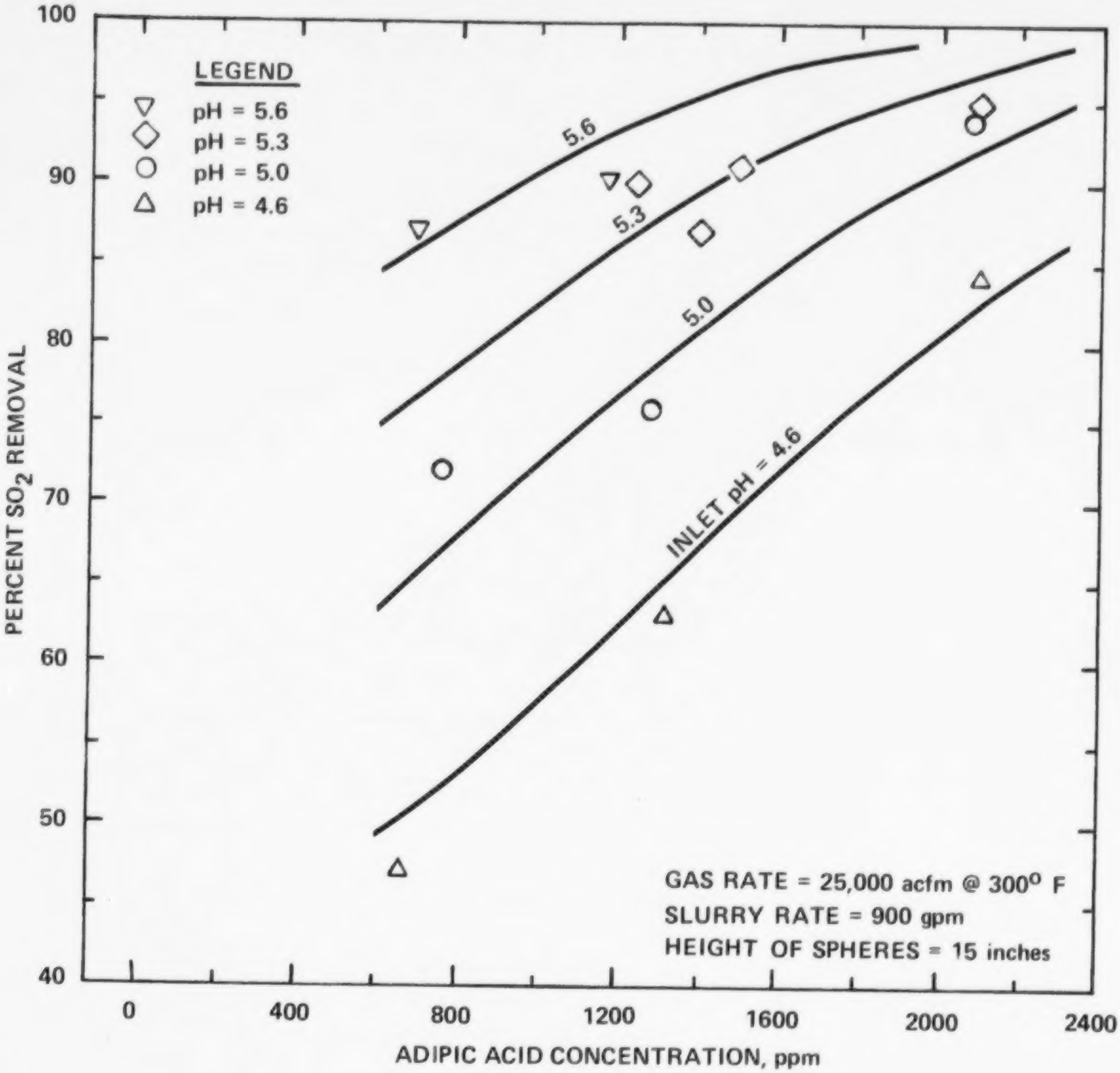

Figure 22-23. Effect Of Adipic Acid Concentration And Scrubber Inlet pH On SO_2 Removal In The TCA With Four Grids And 15 Inches Of Spheres (With Two-Tank Forced Oxidation)

and TCA inlet liquor pH. The lines in Figure 22-23 are predicted by Equation 22-19; the actual data points are also shown.

In comparing Figure 22-23 with Figures 22-21 and 22-22 (high pH data), the low pH curves of Figure 22-23 have a noticeably steeper slope for adipic acid concentration above 600 ppm than is the case for the high pH data. At low pH, the adipic acid is partially ineffective because of significant amounts of un-ionized adipic acid. For example, Figure 22-22 shows that, at 1.2 limestone stoichiometry (inlet pH of 5.6 to 6.1) and 28 gpm/ft^2 (900 gpm), 75 percent SO_2 removal can be achieved with zero adipic acid concentration. To achieve this same 75 percent SO_2 removal, Figure 22-23 shows that 600 ppm of adipic acid is required at 5.3 inlet pH, and 1700 ppm at 4.6 inlet pH.

Therefore, SO_2 removal is sensitive to fluctuations in pH and adipic acid concentration with low pH operation.

Figure 22-24 is a plot of hourly SO_2 removal data as a function of scrubber inlet pH and adipic acid concentration for Runs TAA006, TAA025, TAA028, TAA032, and TAA053 through TAA064. The plot further demonstrates that the SO_2 removal is sensitive to both pH and adipic acid concentration for scrubber inlet pH below about 5.3-5.6.

22.9 TCA WITH LIMESTONE AND LOW INLET SO_2 CONCENTRATION

A total of 14 limestone factorial tests without adipic acid were conducted in August 1979 when the inlet SO_2 concentration was too low (1360-2240 ppm) to obtain any meaningful data for comparison with other high sulfur results.

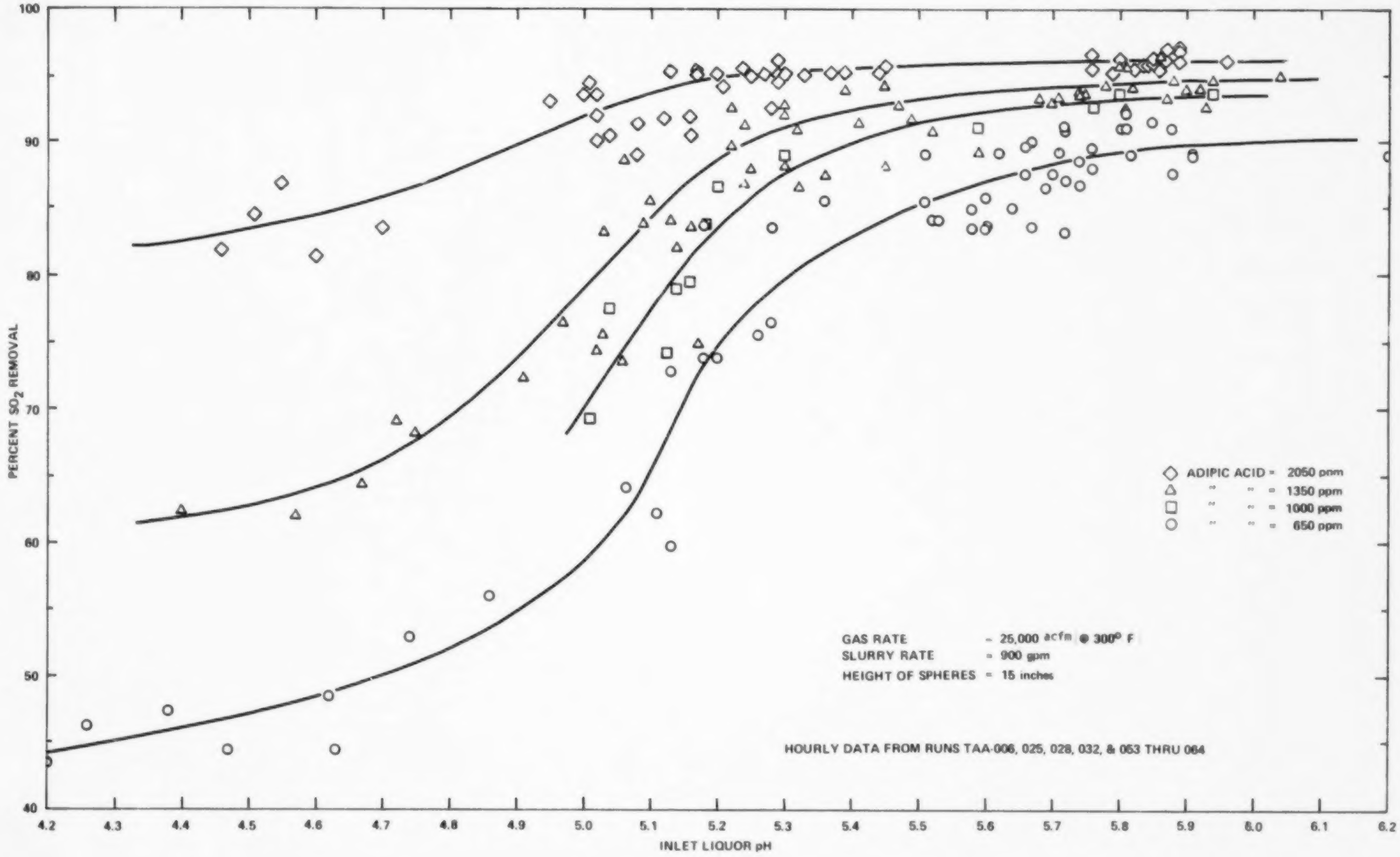

Figure 22-24. Sensitivity Of SO_2 Removal With Variations In Scrubber Inlet pH And Adipic Acid Concentration

Table 22-15

RESULTS OF LIMESTONE FACTORIAL TESTS WITH FORCED OXIDATION USING ONE TANK -LOW INLET SO_2 CONCENTRATION-

Run No.	Gas Rate (acfm)	Liquor Rate (1) (gpm)	L/G gal/Mcf	Press. Drop (in. H_2O)	TCA Inlet Liquor pH		TCA Outlet Liq. pH	Ave $AD^=$ Conc (ppm)	Ave Cl^- Conc (ppm)	LS Utiliz.	Inlet SO_2 Concentration (ppm)		Percent SO_2 Removal		Air Rate (scfm)	Sulfite Oxid. (%)	Spheres (inches)	Replicate
					Range	Ave					Range	Ave	Range	Ave				
TAA301	25,000	894	45	2.3	5.42-5.68	5.58	5.4	0	1338	87	1360-1800	1590	46-52	48.1	220	98.8	0	A
TAA302	25,000	1183	59	2.7	5.44-5.68	5.54	5.6	0	3160	85	1680-1800	1769	59-63	61.9	220	98.1	0	
TAA303	25,000	593	30	1.9	5.66-5.70	5.68	5.5	0	2538	78	1840-2040	1941	38-43	42.0	220	98.8	0	
TAA304	25,000	875	44	2.2	5.56-5.58	5.57	5.3	0	2503	71	1920-2000	1954	54-55	54.6	220	99.3	0	
TAA305	25,000	886	44	2.3	5.65-5.87	5.75	5.5	0	2459	76	1480-1720	1603	58-61	59.6	220	99.5	0	A
TAA306	25,000	1179	59	2.8	5.58-5.77	5.68	5.6	0	2370	70	1800-2000	1918	68-71	69.6	220	99.5	0	
TAA307	25,000	597	30	1.9	5.79-5.86	5.83	5.4	0	3275	61	2200-2240	2225	44-45	44.8	220	99.1	0	
TAA308	25,000	907	45	6.5	5.11-5.30	5.22	5.1	0	2316	89	1740-2100	1976	58-69	61.2	220	99.6	15	B
TAA309	25,000	1203	60	7.5	5.25-5.38	5.31	5.0	0	3994	79	1720-1920	1856	80-84	82.2	220	99.5	15	
TAA310	25,000	593	30	5.5	5.29-5.46	5.39	4.9	0	3181	75	1880-2080	2033	56-59	57.1	220	99.4	15	
TAA311	25,000	893	45	6.4	5.20-5.36	5.30	5.1	0	3846	82	1960-2080	2038	70-73	71.3	220	99.4	15	B
TAA312	25,000	901	45	6.5	5.50-5.68	5.58	5.2	0	3373	63	1880-1960	1911	77-78	77.2	220	98.7	15	
TAA313	25,000	1197	60	7.6	5.25-5.54	5.41	5.2	0	4689	64	1840-2000	1914	83-86	84.7	220	99.6	15	
TAA314	25,000	586	29	5.3	5.13-5.52	5.29	5.0	0	4808	67	1880-2080	1958	59-61	59.5	220	99.4	15	

(1) External downcomer used.

Table 22-15 lists the results of the 14 tests. All runs were made with forced oxidation using one tank (Figures 16-1 and 16-2). The external downcomer of the oxidation tank was used. Common test conditions were:

Fly ash loading: High (2-7 grains/dry scf)
Flue gas flow rate: 25,000 acfm @ 300°F
Slurry solids concentration: 15 percent
Oxidation tank level (7 ft diameter): 17 ft
Air flow rate to oxidizer: 220 scfm
Agitator speed: 54 rpm

The SO_2 removal ranged from a low of 42 percent (Run TAA303 at 593 gpm slurry flow, 78 percent limestone utilization, and no spheres) to a high of 84.7 percent (Run TAA313 at 1197 gpm slurry flow, 64 percent limestone utilization, and 15 inches of spheres).

22.10 SUMMARY

The following is a summary of significant results from the factorial tests:

- A semi-theoretical mathematical model of the form given by Equation 22-6 has been successfully used to correlate the factorial data. The correlations usually explained better than 90 percent of the variation in the data for SO_2 removal, with a standard error of estimate of 2 to 4 percent SO_2 removal.
- A venturi alone can remove 70 percent SO_2 using lime enhanced with about 3100 ppm adipic acid, and operates at an L/G of 37 gal/mcf, 6.0 venturi inlet pH, 9 inches H_2O pressure drop, and 2200 ppm inlet SO_2 concentration.
- No significant difference in SO_2 removal efficiency could be observed between runs using fresh adipic acid and runs using recycled (degraded) adipic acid.
- Forced oxidation in the scrubber loop increases the SO_2 removal efficiency with or without adipic acid. The effect is more pronounced as the scrubber inlet pH is reduced.
- For 90 percent SO_2 removal with the spray tower operating with limestone (without adipic acid) at 5.8 inlet pH, a liquid-to-gas ratio of 120 gal/mcf was required with forced oxidation and 135 gal/mcf without forced oxidation.

Section 23

SUMMARY OF CHARACTERISTICS OF ADIPIC ACID AS A SCRUBBER ADDITIVE

Based on the results of the Shawnee adipic acid test program, as well as other related EPA programs, the characteristics of adipic acid as an additive in a limestone or lime FGD scrubber can be summarized as follows:

- Adipic acid significantly enhances the SO_2 removal efficiency.
- The effective scrubber inlet pH is only approximately 5.2 (higher than the upper pH buffer point of about 5), at which most of the adipic acid is in ionized form and its buffer capacity is more fully utilized.
- At a scrubber inlet pH of 5.2 or higher (effective pH), the optimum concentration range of adipic acid is only 700 to 1500 ppm (5 to 10 m-moles/liter).
- Scrubber inlet pH lower than 5.2 (but higher than the lower pH buffer point of about 4) can be used. However, higher adipic acid concentrations are required to maintain adequate buffer capacity for similar SO_2 removal enhancement.
- At pH levels lower than 5.2, the limestone utilization is usually greater than 85 percent for an adipic acid-enchanced limestone system, as compared to 65-70 percent utilization at the higher pH needed in unenhanced limestone systems to achieve an equivalent SO_2 removal. Thus, an adipic adipic acid-enhanced system consumes less limestone, generates less waste sludge, and improves the overall system economy.
- Higher limestone utilizations in a limestone/adipic acid system contribute to reliable scrubber operation.
- With proper pH control and sufficient adipic acid concentration (sufficient buffer capacity), steady outlet SO_2 concentrations can be maintained even with wide fluctuations of inlet SO_2 concentrations.
- Since limestone dissolution is not a rate-controlling step in SO_2 absorption for an adipic acid-enhanced limestone system, adipic acid should promote use of less expensive and less energy-intensive limestone rather than lime.

- The effectiveness of adipic acid is not affected by forced oxidation and it can be used with both lime and limestone in systems with or without forced oxidation.

- The effectiveness of adipic acid is not adversely affected by chlorides as is the limestone/MgO process. Thus, it is especially attractive for very tightly closed liquor loop operation.

- When used with lime, both good SO_2 removal and sulfite oxidation can be achieved in a single-loop scrubber system using within-scrubber-loop forced oxidation. Under this operating mode, calcium adipate becomes the major SO_2 scrubbing species.

- Forced oxidation within the scrubber loop improves the SO_2 removal efficiency, with or without adipic acid addition. This is true when sulfite is not a major scrubbing species and the SO_2 removal does not depend on the sulfite-bisulfite buffer.

- Adipic acid does not affect the slurry filtration properties. It only reduces somewhat the initial settling rate of oxidized limestone slurry (15 percent solids concentration) from 1.2 to 0.7 cm/min. This is still significantly higher than 0.2 cm/min settling rate for unoxidized limestone slurry with or without adipic acid.

- Adipic acid decomposition, and the indications that it is adsorbed on solids or occluded in solids (Reference 23), requires adding up to 5 times that amount theoretically required. However, the consumption over the ranges anticipated has negligible economic impact.

- Some decomposition products, such as valeric acid, have a noticeable odor. However, this was not a problem.

- The rate of decomposition or degradation of adipic acid is reduced at low pH.* Without forced oxidation, essentially no degradation occurs at a scrubber inlet pH below about 5.0. Both forced oxidation and high limestone stoichiometry (due to limestone blinding) contribute to higher adipic acid degradation.

- Operating a scrubber at low pH and high adipic acid concentration can actually result in lower total adipic acid consumption than operation at a high pH and low concentration for the same SO_2 removal.

- The optimum scrubber inlet pH appears to be 5.0 to 5.1 with respect to adipic acid degradation, limestone utilization, calcium sulfite saturation, and the sensitivity of SO_2 removal to pH and inlet SO_2 concentration.

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*Recent laboratory test results at the University of Texas at Austin (Reference 24) have shown that the adipic acid degradation decreases in the presence of Mn ion, and also decreases with pH when Mn is present. The IERL-RTP pilot plant test results (Reference 25) have also identified Mn ion as possible inhibitor of adipic acid degradation.

- Results from Level 1 bioassay analysis showed no measurable difference in toxicity or mutagenicity between flue gas and slurry samples from limestone scrubbers operating with and without adipic acid (References 18 and 19).

- No noticeable difference in corrosion of materials could be detected between operation with adipic acid at pH 5 and operation without adipic acid at higher pH (5.6-5.8).

Section 24

ECONOMICS OF ADIPIC ACID-ENHANCED LIMESTONE SCRUBBING

The economics of limestone scrubbing, with or without additive, has been projected for forced oxidation systems designed to achieve an average of 90 percent SO_2 removal from high sulfur flue gas. The capital investment and revenue requirements are calculated using a Design-Economics Computer Program which was jointly developed by TVA and Bechtel under the EPA sponsorship (References 26 and 30). The results indicate that, for the cases studied, the capital investments are 4 to 5 percent lower and the operating costs are 5 to 7 percent lower for adipic acid-enhanced limestone systems than for a limestone system without additive. Major savings result from the reduced limestone requirement and the associated grinding operation, and from the reduced quantity of waste solids to be disposed of in adipic acid-enhanced limestone systems. These savings more than offset the cost of adipic acid and its associated handling and feeding operations.

Four cases have been studied including a limestone case with MgO additive. The operating conditions for these cases are presented in Table 24-1. The evaluations are based on a new 500-MW scrubbing facility incorporating forced oxidation and operating on flue gas from a boiler burning eastern coal containing 4 percent by weight sulfur. The cases evaluated are:

- Case 1 - A limestone base case without additive operated at relatively high limestone stoichiometry and liquid-to-gas ratio to achieve 90 percent SO_2 removal. It should be noted that long-term reliability with this mode of operation has not been demonstrated at Shawnee.

Table 24-1

CONDITIONS FOR ECONOMIC ANALYSIS OF LIMESTONE SCRUBBING WITH FORCED OXIDATION AND WITH OR WITHOUT ADDITIVE

Capacity:	500 MW
Coal:	4 wt % sulfur
Scrubber:	TCA with 3 beds, 4 grids, and 5 inches of static height of spheres per bed
SO_2 Removal Efficiency:	90%
Superficial Gas Velocity:	12.5 ft/sec
Number of Trains:	5, including one spare train
Solids Dewatering:	To 80% solids by thickener and rotary drum vacuum filter
Onstream Factor:	5500 hr/yr
Effluent Hold Tank Residence Time:	5 min
Oxidation Tank Residence Time:	5 min
Oxidation Tank Level:	18 ft
Air Sparger Pressure Drop:	5 psi
Oxidation Tank Agitator Hp:	0.002 brake Hp/gal
Solid Sulfite Oxidation:	99%
Air Stoichiometry:	1.7 lb-atoms O/lb mole SO_2 absorbed
Number of Tanks:	2 (effluent hold tank and oxidation tank)
Alkali:	Limestone

Case No.	1	2	3	4
Additive	-	MgO	Adipic Acid	Adipic Acid
Additive Concentration, ppm	-	5500$^{(a)}$	800	2000
Additive Rate, lb/hr	-	104	83.3$^{(b)}$	53.6$^{(c)}$
L/G, gal/mcf	58	50	50	50
Limestone Stoichiometry, moles Ca/mole SO_2 absorbed	1.52	1.20	1.20	1.05
TCA Inlet pH	5.8	5.4	5.6	4.8
Mode of Oxidation	1 loop, 2 tanks	bleed stream	1 loop, 2 tanks	1 loop, 2 tanks

(a) Excess of molar equivalent of chloride.
(b) Five times theoretical consumption.
(c) 1.4 times theoretical consumption.

- Case 2 - A limestone case with MgO addition. Oxidation of the scrubber bleed stream was chosen because in-loop oxidation is incompatible with magnesium-enhanced scrubbing. As in Case 1, long-term reliability has not been demonstrated at Shawnee for this mode of operation.
- Case 3 - A limestone case with adipic acid addition operated at high pH. Although only 800 ppm of adipic acid is required to obtain 90 percent SO_2 removal, degradation of adipic acid at high pH requires about five times the theoretical adipic acid addition rate.
- Case 4 - A limestone case with adipic acid addition operated at low pH. For this case, 2000 ppm adipic acid is required. However, the low pH operation requires only 1.4 times the theoretical adipic acid addition rate and 1.05 limestone stoichiometry.

The results of the economic evaluations are presented in Tables 24-2 and 24-3. The capital investment and the first year revenue requirement in Table 24-2 include the dewatering equipment (thickener and filter) but exclude the waste sludge (filter cake) disposal area. Table 24-3 lists separately the first year revenue requirement for the waste sludge disposal area.

As shown in Table 24-2, both the total capital investment and the first year revenue requirement are the lowest for adipic acid-enhanced limestone scrubbing at low pH (Case 4). The total capital investment is reduced by 4.8 percent and the first year revenue requirement reduced by 5.8 percent for the limestone/adipic acid/low pH case (Case 4) compared with the conventional limestone case (Case 1). The revenue requirement includes 14.7 percent annual capital charge.

Total capital investment and operating costs for adipic acid-enhanced limestone at high pH (Case 3) are higher than those for limestone/adipic acid at low pH (Case 4), but are still lower than those for the conventional limestone (Case 1) or the limestone/MgO case (Case 2). Total capital investment is lower by 3.9 percent and the first year revenue requirement is lower by 4.0 percent for Case 3, compared with Case 1.

Table 24-2

RESULTS OF ECONOMIC ANALYSIS EXCLUDING WASTE SLUDGE DISPOSAL AREA

	Total Capital Investment			First Year Revenue Requirement		
Case No.	$MM(1982)	$/kW	Cost Factor	$MM(1984)	Mils/kWh	Cost Factor
1	87.40	174.8	1.000	25.01	9.09	1.000
2	85.26	170.5	0.975	24.15	8.78	0.966
3	83.97	167.9	0.961	24.01	8.73	0.960
4	83.22	166.4	0.952	23.56	8.57	0.942

Revenue requirement includes 14.7% annual capital charge.

Raw material costs (1984): Limestone - $8.5/ton
MgO - $460/ton
Adipic Acid - $1200/ton

Table 24-3

REVENUE REQUIREMENT IN WASTE SLUDGE DISPOSAL AREA

		First Year Revenue Requirement, Mils/kWh (1984)			
Case No.	Filter Cake, dry tons/hr	Total Excluding Sludge Disposal	Sludge Disposal	Total	Cost Factor
1	48.7	9.09	0.97	10.06	1.000
2	41.6	8.78	0.83	9.61	0.955
3	41.6	8.73	0.83	9.56	0.950
4	38.3	8.57	0.77	9.34	0.928

Revenue requirement includes 14.7% annual capital charges.
Sludge disposal cost assumes $10/dry ton, including 14.7% annual capital charges.

Table 24-3 illustrates the additional savings from adipic acid addition. Because of the lower pH operation, and thus lower limestone consumption, the amount of waste solids produced is lower for limestone/adipic acid cases (Cases 3 and 4) than for a limestone case (Case 1). Assuming a landfill disposal cost of $10/dry ton, including 14.7 percent annual capital charges, the first year revenue requirements for the sludge disposal area are 0.97, 0.83, and 0.77 mills/kWh for Cases 1, 3, and 4, respectively. Thus, the total first year revenue requirement, including the sludge disposal area, is 9.34 mills/kWh for Case 4 compared with 10.06 mills/kWh for Case 1. This is a reduction of 7.2 percent, compared with 5.8 percent when the sludge disposal cost is not included.

These cost figures are cited as representative of typical scenarios only, and some variation from them is normal. Moreover, the differences in total capital investments and operating costs among these cases are small. The principal conclusion from these evaluations is that adipic acid addition decreases cost consistently when using the same comparison basis. Readers who are interested in the details of the design and economic premises are referred to Reference 30.

It should be noted that adipic acid provides greater flexibility in determining fuel choice, limestone type, and control level that other alternatives cannot provide. Many of the economic scenarios provided by the adipic acid may be very advantageous on site-specific cases. Furthermore, in the economic analysis presented above, several important factors which illustrate the advantages of adipic acid were not taken into account. Some of these factors are:

- Low cost, high-sulfur coal can be used in lieu of high cost, low-sulfur coal.
- A spray tower (which is a low efficiency scrubber) can be used, which gives higher reliability and availability and requires less maintenance compared to other scrubber types.

- A smaller effluent hold tank and oxidation tank can probably be used.
- Filter cake washing can be employed, with negligible added expense, to further reduce the adipic acid requirement.

Section 25

LIMESTONE BLINDING BY CALCIUM SULFITE

Blinding of limestone as evidenced by low limestone utilization and/or low pH was encountered during limestone tests with and without adipic acid enhancement.

The limestone blinding was most common under in-loop forced oxidation conditions, where the recirculated slurry was deficient in solid calcium sulfite crystal seeds and the calcium sulfite in the liquor preferentially precipitated on, and blinded, the alkaline limestone particles. This section describes system behavior during limestone blinding, the conditions leading to it, and recommended solutions for eliminating or avoiding limestone blinding.

25.1 SYSTEM BEHAVIOR DURING LIMESTONE BLINDING

Limestone blinding in a scrubber is normally characterized by the following phenomena:

- Severe drop in slurry pH
- Very insensitive pH response to the change in limestone addition rate, even at low pH
- Poor limestone utilization
- High sulfite concentration in the liquor

The first indication of limestone blinding is a precipitous drop in the pH of the recirculating slurry for no apparent reason. In order to control system pH, the operator normally begins to increase the limestone feed rate, leading to poor limestone utilization. Limestone utilization as low as 20 to 25 percent was observed at Shawnee. While the pH response to the limestone feed rate is normally more sensitive at a low pH range of 4.5 to 5.5 (less limestone buffer) than at a high pH range of 5.5 to 6.5 (more limestone buffer), the response is typically sluggish even at low pH when limestone blinding occurs.

Limestone blinding is usually accompanied by high sulfite concentration (high sulfite saturation) in the scrubber liquor. In forced oxidation systems, or systems with very high natural oxidation, this is usually the result of insufficient calcium sulfite solid seeds for sulfite precipitation and desupersaturation. The sulfite thus accumulated in the liquor precipitates preferentially on the alkaline limestone particles, causing the blinding. Insufficient oxidation intensity in the liquor tends to increase the liquor sulfite concentration. High sulfite saturation or concentration could also be caused by high SO_2 make-per-pass, leading to limestone blinding in the scrubber effluent line.

In the case of lime scrubbing with forced oxidation, where blinding of lime is unlikely, high sulfite saturation would undoubtedly cause calcium sulfite scaling (see Section 16).

25.2 CONDITIONS LEADING TO LIMESTONE BLINDING

The necessary conditions for blinding to occur are:

- Slurry solids deficient in calcium sulfite crystal seeds
- High sulfite concentration and/or supersaturation in the slurry liquid

The slurry solids deficient in calcium sulfite crystal seeds (i.e., high gypsum content) can be a result of forced oxidation or high natural oxidation. Experience at Shawnee indicates that limestone blinding does not occur at sulfite oxidation levels in solids below approximately 85 percent under most of the operating conditions.

When the slurry solids contain an insufficient amount of calcium sulfite crystals, the saturated sulfite in the liquor tends to precipitate preferentially on alkaline solid particles such as limestone, because the solubility of calcium sulfite is a strong function of pH and decreases with increasing pH. Thus, even if the bulk liquor is not supersaturated with sulfite, as may be the case with low bulk liquor pH, supersaturation and precipitation could occur in the high pH region in the vicinity of the limestone particles, causing blinding.

The following modes of operation can create a recirculated scrubber slurry which is high in gypsum content and low in calcium sulfite seed crystals:

- Single-loop operation with in-loop forced oxidation
- Two-loop operation with forced oxidation in the first scrubber loop
- Bleed stream oxidation with a recycle stream to the main scrubber loop
- High natural oxidation in the scrubber loop

High sulfite concentration or supersaturation can be caused by:

- Insufficient oxidation intensity, even though sulfite oxidation in the solids may be nearly complete (affecting both scrubber inlet and outlet liquors)
- High SO_2 make-per-pass (affecting scrubber outlet liquor)

The use of additives, such as adipic acid, enhances the SO_2 removal and increases the SO_2 make-per-pass, thus increasing the potential for limestone blinding.

25.3 RECOMMENDED SOLUTIONS

Operating Considerations. Limestone blinding by calcium sulfite is the result of calcium sulfite-deficient slurry solids (high gypsum content) and high calcium sulfite supersaturation (or high sulfite concentration) in the liquor. The latter can be caused by insufficient oxidation intensity, high SO_2 make-per-pass, or both.

Therefore, any measures that can reduce these effects will reduce the chance of limestone blinding. Better oxidation can be obtained by:

- Increasing the air stoichiometry
- Increasing the oxidation tank level to provide a longer air bubble residence time
- Increasing the oxidation tank agitation

This would reduce the sulfite saturation and concentration at the scrubber inlet.

The level of sulfite in the scrubber effluent liquor can be reduced by reducing the inlet liquor sulfite as above or by reducing the SO_2 make-per-pass. Lower SO_2 make-per-pass can be obtained by lowering the flue gas throughput, increasing the slurry flow rate, or both.

Design Considerations. If an in-loop forced oxidation system with a single tank is desired, then provision should be made:

- To provide an adequate oxidation intensity to minimize sulfite saturation at the scrubber inlet
- To reduce SO_2 make-per-pass (outlet sulfite concentration)

A better solution appears to be the use of two tanks in series, which provide several advantages over the single-tank mode listed in Section 10.

Limestone blinding in the long scrubber effluent line (see Sections 4, 9, and 10), which functioned as a plug-flow reactor, was unique at Shawnee. Under the condition of high SO_2 make-per-pass (or high sulfite concentration in the scrubber effluent liquor), the plug flow reactor tended to facilitate calcium sulfite precipitaiton. The precipitation led to limestone blinding when the slurry was deficient in calcium sulfite crystal seeds. Therefore, in full-scale design, the scrubber effluent piping should be as short as possible to minimize the potential for limestone blinding.

Section 26

SLURRY SETTLING AND FILTRATION PROPERTIES

Initial settling rates and sludge dewatering characteristics were routinely monitored in the Shawnee laboratory by graduated cylinder settling tests and Buchner vacuum funnel filtration tests. Appendix L presents the results of the tests that were performed from July 1978 through March 1981. Table 26-1 summarizes the results given in Appendix L.

Initial settling rate from the graduated cylinder settling test indicates the rate at which the solids fall during the unhindered portion of settling. Ultimate settled solids concentration from the cylinder test represents the highest achievable solids concentration in a thickener underflow or in a settling pond. Buchner funnel filtration test cake solids concentration represents that achievable on a filter type dewatering device.

As reported previously (Reference 6), settling and filtration characteristics of oxidized slurry are superior to those of unoxidized slurry. The same condition exists with the slurry samples containing adipic acid.

With initial solids content of about 15 percent, the average initial settling rate for all oxidized limestone slurry with high fly ash loading decreased from about 1.2 cm/min with no adipic acid to about 0.7 cm/min with adipic acid. This latter rate was still considerably higher than settling rates without

Table 26-1

SUMMARY OF THE SLURRY SETTLING AND FILTRATION PROPERTIES

Oxidation	Fly Ash Loading	Alkali	Slurry Solids wt%	Oxidation Scheme	No. of Tanks in Oxid. Loop	Adipic Acid Conc. ppm	Initial Settling Rate cm/min avg.	Initial Settling Rate cm/min range	Ultimate Settled Solids wt% avg.	Ultimate Settled Solids wt% range	Funnel Test Cake Solids wt% avg.	Funnel Test Cake Solids wt% range	No. of Samples
Yes	High	LS	15	1-loop	1	3030	0.7	0.4-1.0	66	57-82	70	63-74	14
Yes	High	LS	15	1-loop	1	-	1.1	0.5-2.1	65	48-82	69	58-73	36
Yes	High	LS	15	1-loop	2	1600	0.8	0.2-2.7	69	57-86	70	64-77	135
Yes	High	LS	15	1-loop	2	-	1.5	0.3-2.5	69	52-84	73	70-77	45
Yes	High	LS	15	2-loop	2	2200	0.5	0.1-1.9	68	39-83	65	59-77	82
Yes	High	LS	13	2-loop	2	-	1.0	0.8-1.2	70	65-76	72	71-74	5
Yes	High	LS	17	Bleed Stream	-	2100	0.8	0.1-1.9	72	49-88	66	47-76	13
Yes	Low	LS	10	1-loop	1	2300	0.8	0.4-1.8	67	53-97	67	62-73	13
No	Low	LS	10	-	-	1700	0.5	0.2-0.7	39	32-50	41	34-47	10
No	High	LS	15	-	-	1700	0.2	0.1-0.4	50	36-69	56	47-75	169
No	High	LS	14	-	-	-	0.2	0.1-0.4	47	39-60	53	52-66	45
Yes	High	L	8	1-loop	1	1260	1.7	1.5-1.9	55	52-60	60	56-69	6
Yes	High	L	16	2-loop	2	1500	0.4	0.1-0.7	62	55-70	69	64-72	6
Yes	High	L	16	2-loop	2	-	0.2	0.1-0.2	66	62-71	71	71-72	4
No	High	L	8	-	-	1060	1.3	0.4-2.9	49	32-68	55	44-81	11
No	High	L	8	-	-	-	1.4	0.5-2.1	50	38-59	58	48-74	43

NOTE: Values for forced oxidation runs exclude data with solids oxidation less than 90 percent.

forced oxidation. Without forced oxidation, the initial settling rate averaged 0.2 cm/min with or without adipic acid.

For limestone slurry, adipic acid had little or no effect on ultimate settled solids concentration or funnel test cake solids concentration. The average ultimate settled solids concentration operating with forced oxidation and adipic acid addition was 69 percent compared to 67 percent operating without adipic acid. The funnel test cake solids averaged 68 percent with adipic acid and 71 percent without adipic acid for oxidized slurry.

As can be seen in Table 26-1, the oxidation scheme did not have a significant effect on the initial settling rate, the ultimate settled solids, or the funnel test cake solids.

In addition to the Buchner vacuum funnel filtration tests, the filter cake solids from the rotary drum vacuum filter and the belt filter were monitored (see Appendix L). During forced oxidation with adipic acid-enhanced limestone, the drum or belt filter cake solids concentration ranged approximately from 80 to 90 weight percent solids. This range was no different than that obtained when operating with oxidized sludge in the absence of adipic acid.

In summary, adipic acid does not affect the filtration properties of the waste sludge. It reduces the initial settling rate of oxidized limestone slurry from about 1.2 to 0.7 cm/min. However, the reduced rate is still 3 to 4 times higher than the 0.2 cm/min settling rate for unoxidized limestone slurry.

Section 27

FLUE GAS CHARACTERIZATION FOR PARTICULATE AND SULFUR TRIOXIDE

Flue gas characterization was a routine program to determine particulate mass loading, size distribution of particulate matter, and sulfuric acid vapor (SO_3) concentration in the flue gas. The results of testing performed during the reporting period are presented here. Detailed operating conditions such as pressure drop and gas and liquor flow rates are presented in Appendices E through J.

27.1 SAMPLING LOCATIONS

Samples were taken from both the inlet and outlet of each scrubber. The duct at these locations was 40 inches in diameter. Two eight-point traverses, 90° apart, were performed for each mass loading and size distribution test. The inlet sample ports were located upstream of the scrubber inlet where the gas temperature was approximately 300°F. The outlet sample ports were located after the reheater at the scrubber outlet where the gas temperature was approximately 250°F. The sample ports were located about two duct diameters upstream and six duct diameters downstream of the nearest obstruction.

27.2 TEST METHODS

The procedure used for measuring particulate mass loading was a modification of EPA Method Five. A Hi-Volume sampling train manufactured by the Aerotherm

Division of Acurex Corporation was used. The major differences in test conditions between sampling at Shawnee and a typical Method Five application were: (1) increased sampling flow rate (2 cfm versus 0.75 cfm, typical for EPA Method Five), (2) filter temperatures in the 350°F to 400°F range to prevent acid (SO_3) condensation, and (3) the first two impingers filled with Na_2CO_3 solution to remove SO_2 and to provide corrosion protection for the pump and dry gas meter.

Particulate size distributions were measured with out-of-stack heated inertial impactors. A Brink Model BMS-11 impactor was used for inlet sampling and a Meteorology Research Inc. (MRI) Model 1502 impactor was used for outlet sampling.

To obtain representative size distribution measurements, sampling traverses were made. The flow rate through the impactor was held constant to ensure consistent impactor stage cut sizes. The sampling nozzle was chosen to provide average duct velocity at the nozzle inlet. Because of the uniformity of the duct velocity profile, isokinetic sampling rate was maintained within ±10 percent by sampling at the average duct velocity.

The vapor phase concentration of SO_3 was measured using a controlled condensation technique (Goksoyr Ross). The sample was drawn from a single point approximately one foot inside the stack. The sampled gas was cooled by means of a modified Graham condenser until essentially all the SO_3 condensed, but the temperature of the gas was kept above the water dew point to prevent any interference from SO_2 while a heated quartz filter system removed particulate matter. The condensed acid was then titrated with NaOH, using bromphenol blue as the indicator.

27.3 TEST RESULTS

27.3.1 Mass Loading

The results of mass loading tests are presented in Tables M-1 through M-4 of Appendix M.

Inlet mass loading for the venturi/spray tower (high fly ash loading) ranged from 2.4 to 6.7 gr/dscf, with an average of 3.8 gr/dscf. The range for the outlet mass loading was 0.026 to 0.060 gr/dscf with an average of 0.042 gr/dcsf.

Inlet mass loading for the spray tower system (high fly ash loading) without the venturi ranged from 2.7 to 6.1 gr/dscf with an average of 4.2 gr/dscf. The range for the outlet mass loading for this system was 0.047 to 0.108 gr/dscf with an average of 0.066 gr/dscf.

The TCA mass emissions were generally higher than the venturi/spray tower but lower than the spray tower without the venturi. Operating with high fly ash loading, the average outlet mass loading for the TCA system was 0.061 gr/dscf. For the TCA system operating with low fly ash loading (0.13 to 0.83 gr/dscf at the inlet) the average outlet mass loading was 0.023 gr/dscf.

Outlet mass loadings on the venturi/spray tower decreased as venturi pressure drop increased, as expected. For example, during Run 911-1A, venturi pressure drop averaged 7.0 in. H_2O and the outlet mass loading averaged 0.045 gr/dscf.

The higher pressure drop in Run 907-1A, which averaged 8.5 in. H_2O, lowered the outlet mass loading to an average of 0.042 gr/dscf, and in Run 903-1A, average venturi pressure drop was 9.0 in. H_2O, with the outlet mass loading falling to an average of 0.039 gr/dscf.

The TCA showed a similar relationship between pressure drop and outlet mass loading. For example, Run 902-2A, operating at a pressure drop of 5.8 in. H_2O, had outlet mass loadings averaging 0.059 gr/dscf, whereas during Run 625-2A, when the pressure drop averaged almost 10.0 in. H_2O, the outlet mass loading fell to 0.034 gr/dscf.

Results from the Glitsch Grid Packing test runs (with high fly ash loading) on Train 200 showed very good particulate removal. With the exception of Run TGG109 (which had a very low pressure drop of 1.9 in. H_2O), the average outlet mass loading was 0.038 gr/dscf.

Mass emissions for both trains consistently exceeded the revised EPA New Source Performance Standards for coal fired power plants (0.03 $lb/10^6$ Btu or 0.016 gr/dscf assuming 30 percent excess air in the flue gas) when flue gas with high fly ash loading was used. For only three tests on the TCA system with low fly ash loading was this standard met.

27.3.2 Size Distribution

Inlet and outlet mass loadings as a function of aerodynamic particle size were calculated from the raw impactor data, and plotted in Figures M-1 through M-17.

The figures show that inlet size distributions were similar regardless of scrubber systems, as would be expected. Outlet differential mass loadings for the venturi/spray tower were slightly lower than for the runs with only the venturi. Spray tower-only outlet differential mass loadings were the highest.

27.3.3 Mass Penetration

Particle mass percent penetration (100 minus percent removal) as a function of size was calculated for runs where simultaneous inlet and outlet size distributions were available, and the results are presented in Figures M-18 through M-27. Mass penetration for the venturi/spray tower was slightly higher than for the venturi alone, especially in the range above 2 microns. This is presumably due to slurry or mist eliminator wash water entrainment from the spray tower. Mass penetration for the TCA was higher than for the venturi/spray tower, reflecting the lower particulate removal efficiency of the TCA. Particle penetration for both systems became significant in the range less than 1 micron, where it varied from 25 to 95 percent.

27.3.4 Sulfuric Acid Vapor (SO_3)

The results of SO_3 measurements are presented in Figure 27-1. Inlet SO_3 concentrations averaged 16.6 ppm for Train 100 but only 5.8 ppm for Train 200. The difference may have been due to air leakage in the inlet flue gas duct or because flue gas for the scrubbers was drawn from different parts of Boiler No. 10 or both.

Outlet SO_3 concentrations averaged 6.5 ppm for Train 100 and 2.0 ppm for Train 200. This corresponds to an average SO_3 removal of 61 percent for Train 100 and 66 percent for Train 200. This shows that sulfuric acid vapor was not generated by the scrubbing process.

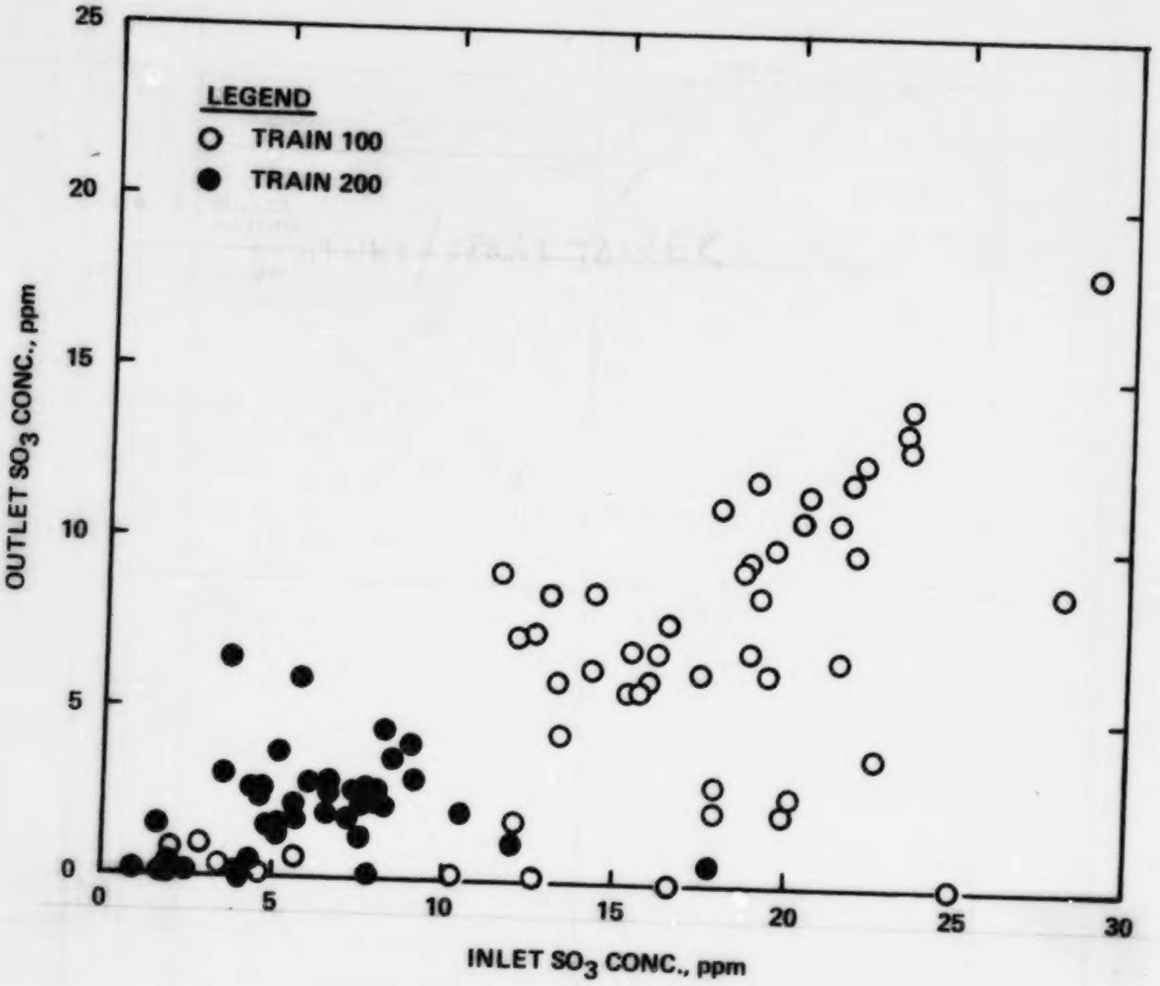

Figure 27-1

SO_3 Inlet Versus Outlet Concentration

Section 28

CORRELATION OF TCA PRESSURE DROP

Mobile spheres used in the TCA tests in this reporting period were 1-7/8 inch diameter, 11.5-gram nitrile foam spheres, except for the Springfield simulation tests (see Section 20) in which 38-mm diameter, 6-gram high density polyethylene spheres were used.

This section presents the data on the pressure drop across three beds of 1-7/8 inch diameter, 11.5-gram nitrile foam spheres. Correlations are also given for the pressure drop as a function of the total static height of spheres and the gas and slurry flow rates. Correlations for the high density polyethylene spheres have been reported elsewhere (References 1 and 2).

28.1 TCA BED PRESSURE DROP TESTS

A series of pressure drop and flooding tests was conducted on the TCA system in mid-November 1978, using 11.5-gram, 1-7/8 inch diameter nitrile foam spheres. The purpose of these tests was to determine the pressure drop and flooding characteristics of the TCA system using the heavier and larger size spheres.

These tests were conducted during the initial part of TCA lime Run 625-2A (see Section 15) before liquid phase equilibrium was reached for the run. Flue gas with high fly ash loading, nominally at 300°F, and a slurry solids concentration of about 15 percent were used.

The TCA consisted of three beds of spheres held in place by four bar grids (3/8 inch diameter, 316L stainless steel bars, 1-1/4 inch on centers). Static bed heights were set at 0, 5, 7.5, and 10 inches per bed with three beds total during these tests. The bar grids were about 4 ft apart. For each bed height, slurry flow rates were adjusted to 800, 1100, 1400, and 1700 gpm. For each slurry flow rate, the gas flow rates were adjusted to 15,000, 20,000, 25,000, and 30,000 acfm at 300°F. These gas flow rates correspond to superficial gas velocities of 6.3, 8.4, 10.4, and 12.5 ft/sec at the nominal scrubber temperature of 125°F. At least two pressure drop measurements across the three beds were taken for each set of conditions.

Pressure drop across the beds increased with increasing bed height, increasing slurry flow rate, and increasing gas rate. Figures 28-1 through 28-4 show the relationships of pressure drop with various gas and slurry rates for bed heights of 0, 5, 7.5, and 10 inches of spheres per bed, respectively. Each data point on these graphs represents the average of two or more measurements.

Flooding occurred at bed pressure drops greater than about 10 inches of H_2O. Flooding was apparent when the pressure drop curve rose sharply. Pressure drop measured during flooding conditions showed erratic and rapid fluctuations.

28.2 TCA PRESSURE DROP CORRELATIONS

One hundred eleven data points (Figures 28-1 through 28-4) were used to fit bed pressure drop as a function of superficial gas velocity, slurry flow rate, and total bed height. Various models were tested to fit the data.

Closed-form models were tried first. These models are consistent with the boundary conditions and will predict zero pressure drop when the gas velocity equals zero. This type of model did not correlate well for the case with spheres,

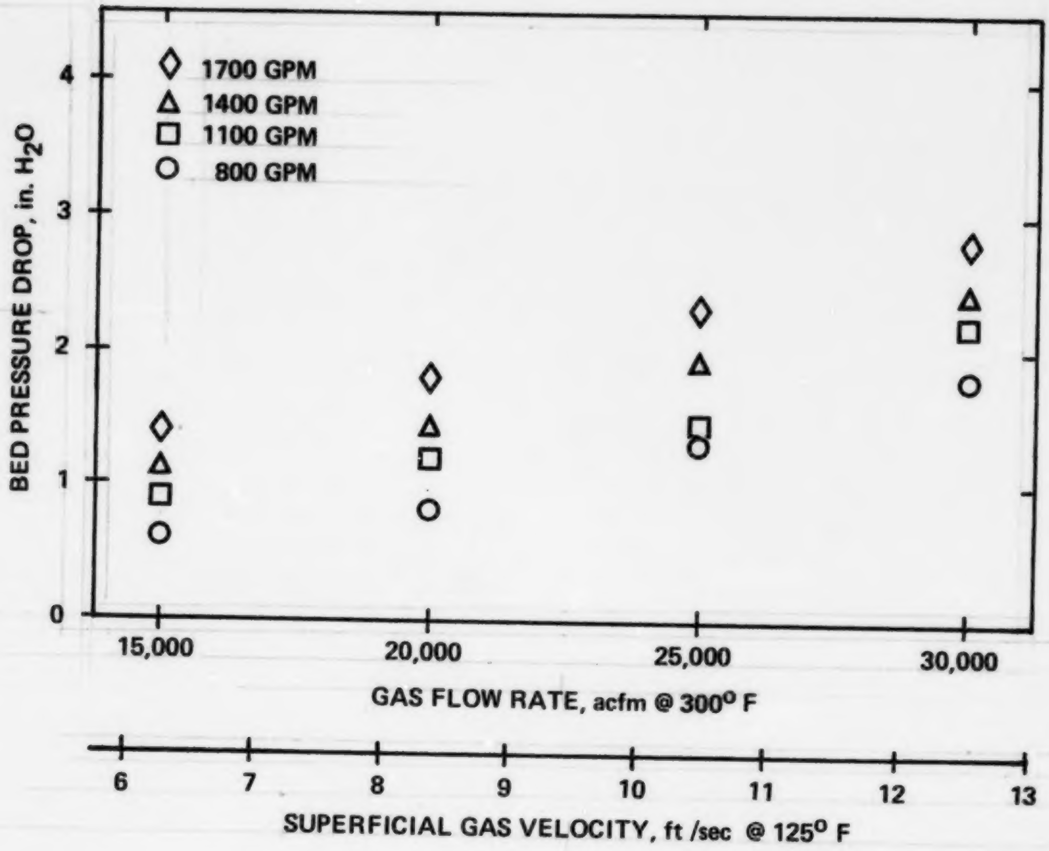

Figure 28-1

Pressure Drop Across The Four-Grid TCA Without Spheres

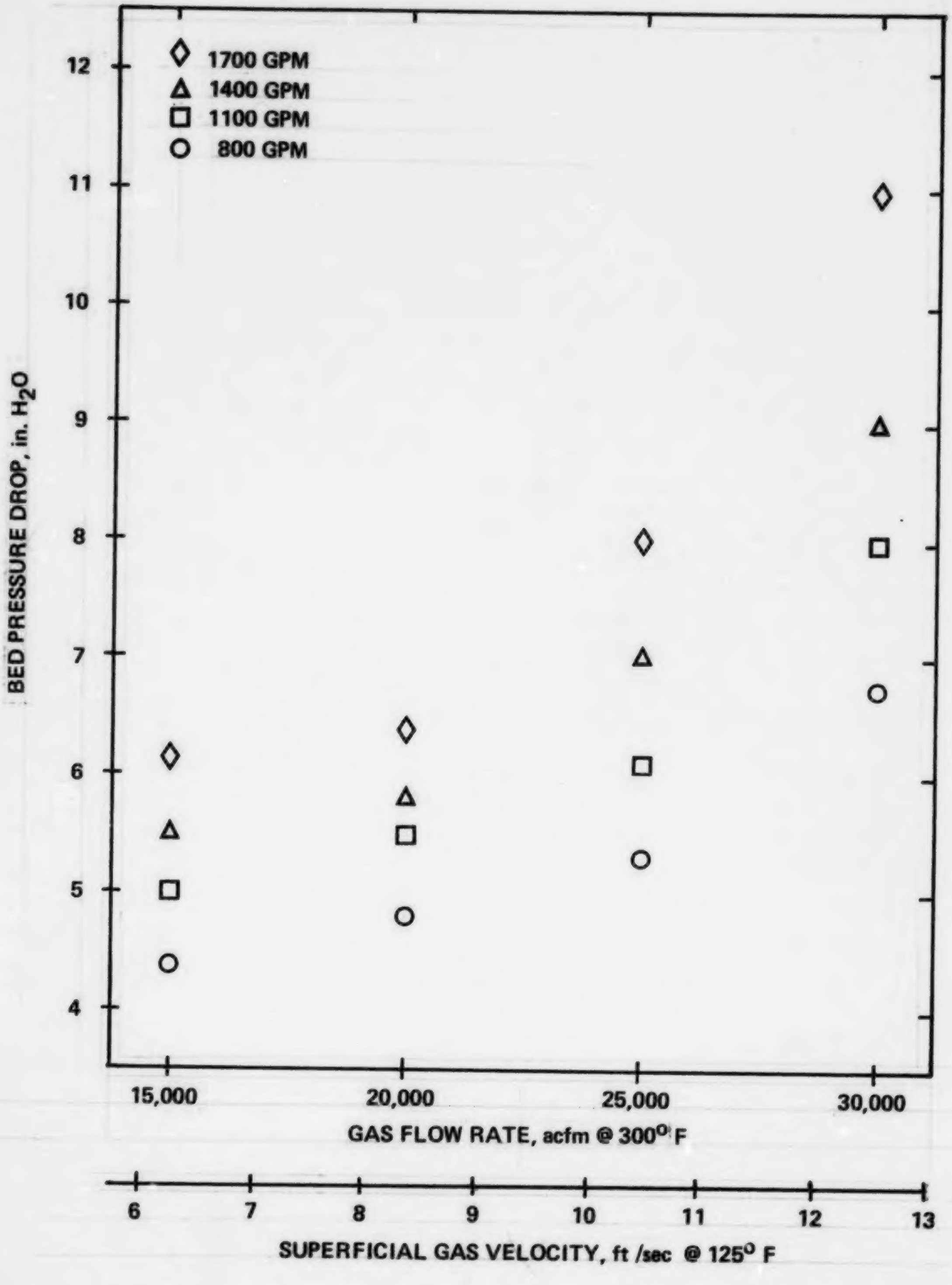

Figure 28-2

Pressure Drop Across The Four-Grid Three-Bed TCA
With 5 Inches Of 11.5-Gram Nitrile Foam Spheres Per Bed

8-4 300

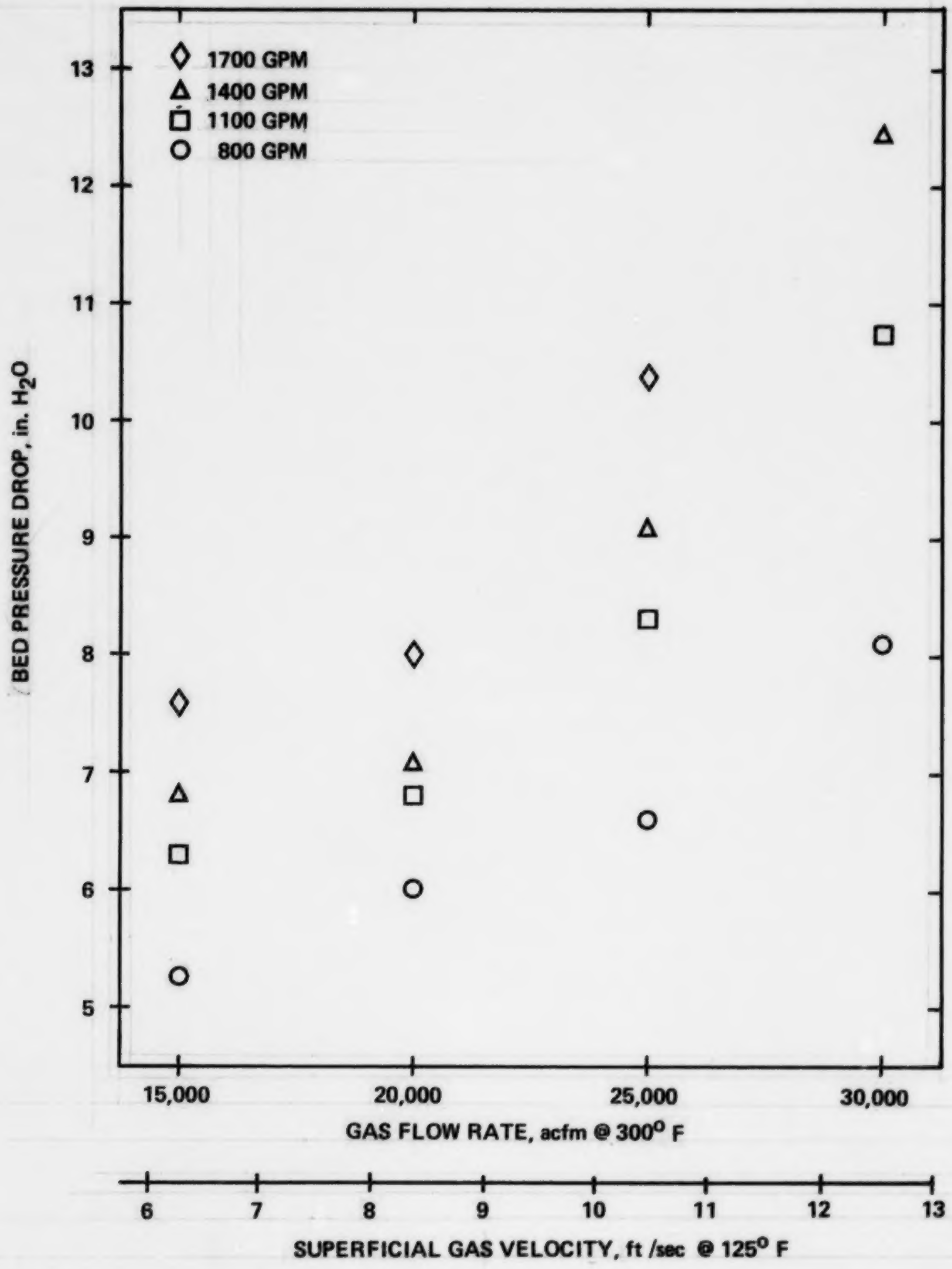

Figure 28-3

Pressure Drop Across The Four-Grid Three-Bed TCA
With 7.5 Inches Of 11.5-Gram Nitrile Foam Spheres Per Bed

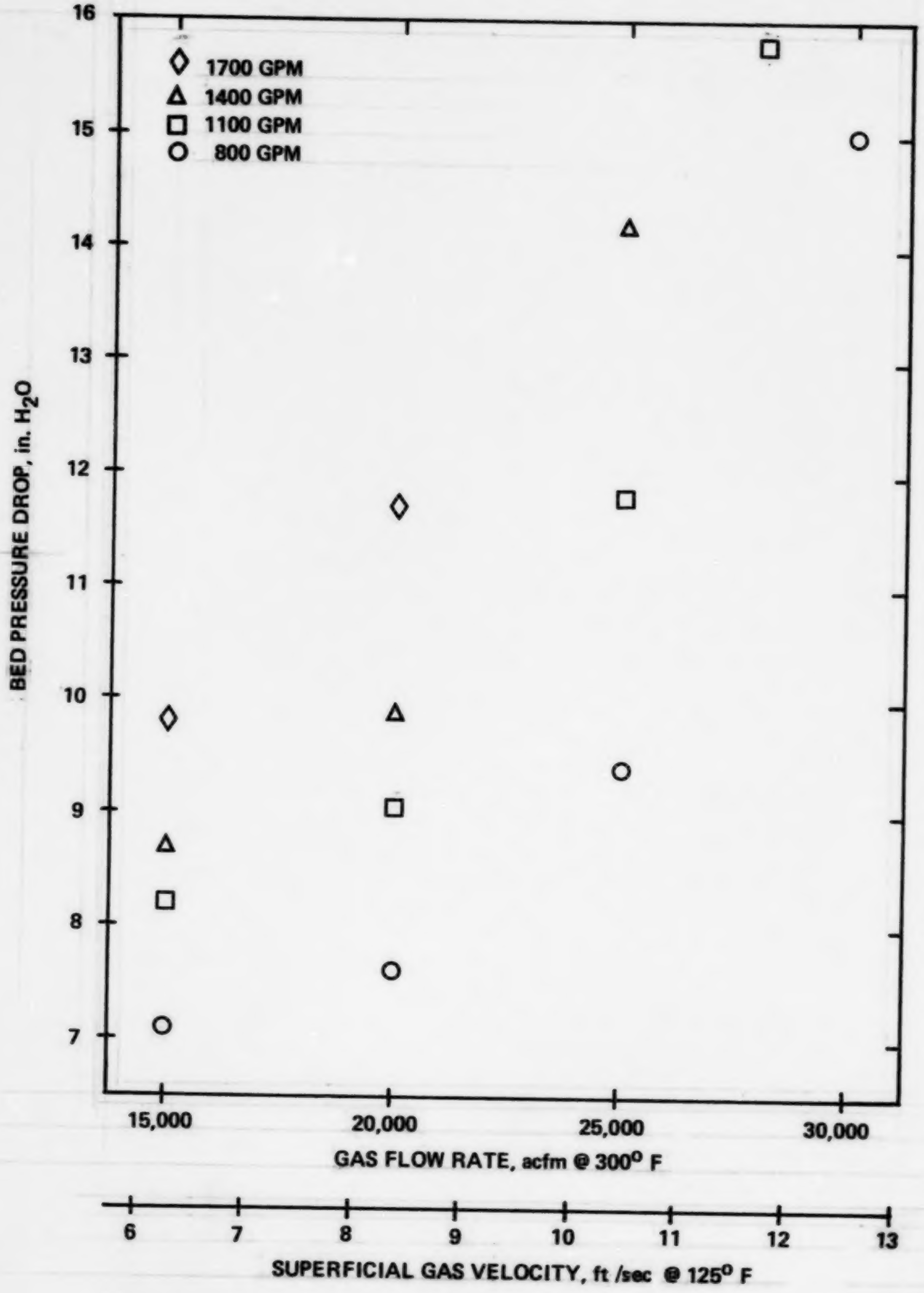

Figure 28-4

Pressure Drop Across The Four-Grid Three-Bed TCA
With 10 Inches of 11.5-Gram Nitrile Foam Spheres Per Bed

and therefore was not used for this case. It did correlate well for the case without spheres, explaining better than 95 percent of the variation in the data with a standard error of estimate of 0.092 inch H_2O. Figure 28-5 shows the relationship of predicted versus measured pressure drop for the following equation generated for the TCA system with only the four bar grids present (Figure 28-1):

$$(\Delta P)_{NS} = 0.0376\ v^{1.245} \exp(0.0233L) \qquad (28\text{-}1)$$

where:

$(\Delta P)_{NS}$ = TCA pressure drop across the four grids (no spheres), inches H_2O*

v = superficial gas velocity, ft/sec (saturated at 125°F)

L = slurry (15 wt%) flow rate per unit scrubber cros-sectional area, gpm/ft^2**

The fitted ranges of variables for Equation 28-1 are:

$(\Delta P)_{NS}$ = 0.6 to 3 inches H_2O

v = 6.3 to 12.5 ft/sec

L = 25 to 53 gpm/ft^2

When correlating the bed pressure drop for 79 data points obtained with spheres present, open-form relationships gave better results for the range of conditions evaluated. A simple sum-of-effects model was tested and proved to be as good or better than any other model tested. Equation 28-2 below explained 91 percent of the variation in the data with a standard error of estimate of 0.41 inch H_2O. The pressure drop without spheres was calculated from Equation 28-1 and then subtracted from the measured pressure drop with spheres to obtain the following expression which gives pressure drop due solely to the height of spheres:

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* Measured from below the bottom grid to above the top grid

** TCA cross-sectional area is 32 sq ft

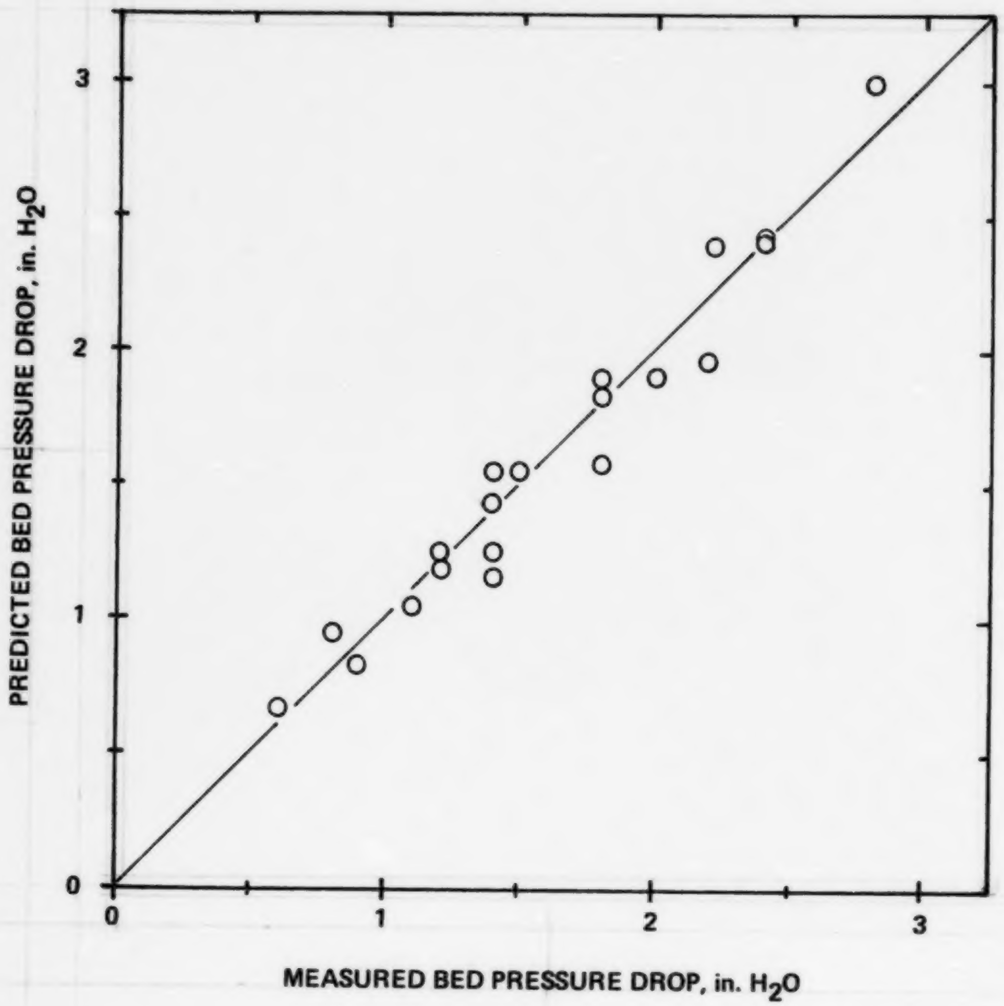


Figure 28-5

Comparison of Experimental Data And Predicted Values (Equation 28-1) Of TCA Bed Pressure Drop Without Spheres

$$(\Delta P)_S = -3 + 0.272\ v + 0.047L + 0.22Hs \qquad (28\text{-}2)$$

where:

Hs = total static bed height of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres in 3 beds, inches

$(\Delta P)_S$ = pressure drop across three beds of spheres minus the effect of the four bar grids, inches H_2O

The fitted range for Hs in Equation 28-2 was 15 to 30 inches. Total bed height had the most significant effect on pressure drop for the range of variables tested.

By combining Equations 28-1 and 28-2, which predict the pressure drop across four bar grids only and the pressure drop for the spheres only, respectively, the total pressure drop across the 3 beds can be calculated. Equation 28-3 below, applicable with spheres present, explained better than 92 percent of the variation in the data with a standard error of estimate of 0.4 inch H_2O for the range of variables tested.

$$(\Delta P)_T = (\Delta P)_{NS} - 3 + 0.272v + 0.047L + 0.22\ Hs \qquad (28\text{-}3)$$

where:

$(\Delta P)_T = (\Delta P)_{NS} + (\Delta P)_S$ = total bed pressure drop including four bar grids and spheres, inches H_2O

Figure 28-6 shows the correlation between the predicted and measured total TCA bed pressure drops.

Equation 28-3 should not be used for total pressure drop, $(\Delta P)_T$, greater than 10 inches H_2O. Flooding of the TCA beds is likely at a pressure drop higher than 10 inches H_2O. The applicable ranges of Hs, v, and L in Equation 28-3 are the same as those in Equations 28-1 and 28-2.

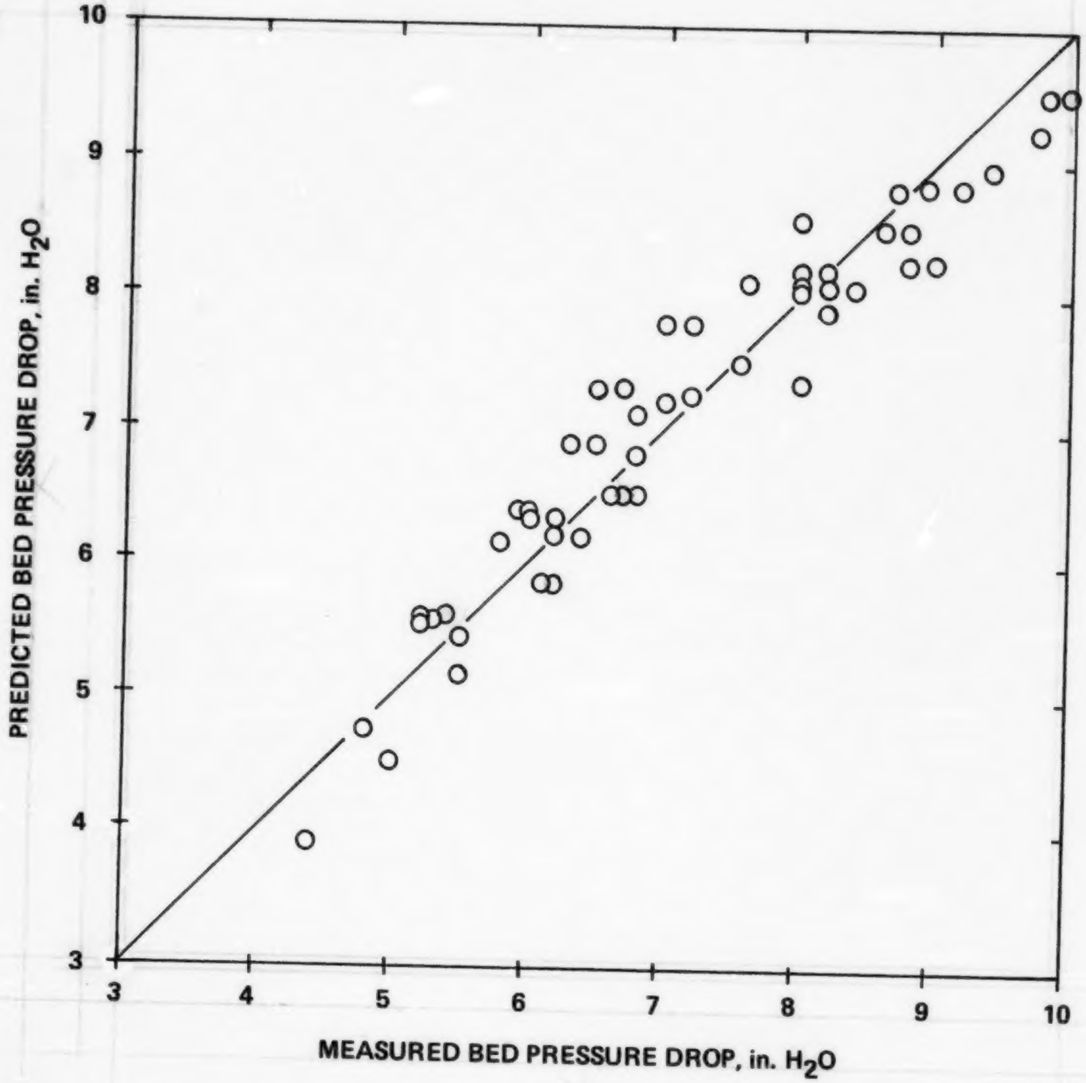


Figure 28-6. Comparison of Experimental Data and Predicted Values (Equation 28-3) of Total Bed Pressure Drop with Spheres

Section 29

MODIFIED EQUATION FOR CALCULATING LIQUID PHASE IONIC IMBALANCE FROM ANALYTICAL DATA

A simplified equation for calculating the liquid phase ionic imbalance has been used in the Shawnee laboratory where the Bechtel modified equilibrium computer program (Appendix K) was not readily accessible. This equation has been used to predict the liquid ionic imbalance from the laboratory-measured dissolved species concentrations to comply with the ± 15 percent liquid ionic imbalance criterion that was set up as part of the quality assurance guidelines (see Section 2.5.2).

Over the years, particularly during the later part of this reporting period, certain modifications had to be made to the original equation (see Section 12, Reference 4) which contained only measured concentrations of Ca^{++}, Mg^{++}, Na^{+}, K^{+}, $SO_3^{=}$, $SO_4^{=}$, and Cl^{-}. These modifications are reflected in the following revised equation:

$$IB = 100\,(1 - Neg/Pos) \qquad (29\text{-}1)$$

where:

IB = percent ionic imbalance

Neg = sum of the equivalence of negative-charged ions

$$= \frac{[SO_4^{=}]}{48.03} + \frac{[TOS] \text{ as } SO_3^{=}}{80.06} \times \left[1 + \frac{6.24 \times 10^{-8}}{6.24 \times 10^{-8} + 10^{-pH}}\right]$$

$$+ \frac{[Cl^{-}]}{35.45} + \frac{[AD] \times FAD}{146.10} + \frac{[TS] - [SO_4^{=}] - [TOS] \text{ as } SO_4^{=}}{96.06}$$

Pos = sum of the equivalence of positive-charged ions

$$= \frac{[Ca^{++}]}{20.04} + \frac{[Mg^{++}]}{12.16} + \frac{[Na^{+}]}{22.99} + \frac{[K^{+}]}{39.10}$$

[ ] = concentrations in ppm by weight

TOS = total oxidizable sulfur (as SO_3 or as SO_3), including only sulfite and bisulfite

TS = total sulfur (as SO_4), including TOS, $SO_4^{=}$, and "hard to oxidize" sulfur species (such as dithionate)

AD = adipic acid/adipate concentration

FAD = ionization factor of adipic acid

= 0, for $pH < 3.5$

= pH - 3.5, for $3.5 \leqq pH \leqq 5.5$

= 2, for $pH > 5.5$

The effect of pH on sulfite/bisulfite equilibrium was not previously included in the equation. This has resulted in erroneously high negative values of calculated ionic imbalance under conditions of low pH and high TOS, because TOS, as determined, is expressed as divalent $SO_3^{=}$ without proper allowance for univalent HSO_3^{-}. The pH term in Equation 29-1 properly accounts for the pH effect. The value of 6.24×10^{-8} is the equilibrium constant for the sulfite/bisulfite shift (Reference 27).

The adipic acid/adipate species (AD) has been added to Equation 29-1 so that the equation is applicable to adipic acid-enhanced scrubber liquor. The factor FAD gives the effect of pH on the ionization of adipic acid, which varies between 0 and 2 for un-ionized and completely ionized acid, respectively.

A new sulfur species, which is "hard to oxidize", has been included in Equation 29-1. This species is added implicitly in the equation as TS minus the sum of $SO_4^=$ and TOS (the last term of Neg), and is expressed in terms of sulfate. This "hard to oxidize" sulfur species is believed to be dithionate ($S_2O_6^=$) and could be oxidized using a more vigorous oxidation procedure with H_2O_2 and HCl digestion. The procedure determines the total sulfur (TS), from which $SO_4^=$ and TOS are subtracted to give the value of "hard to oxidize" sulfur. This extra sulfur species may be the product of forced oxidation, whose effect on the calculated ionic imbalance had not been significant until recently when the scrubber systems were operated mostly under tighter liquor loop closure and lower chloride concentrations.

The tighter liquor loop closure generally experienced in the later part of the reporting period (85-90 percent by weight filter cake solids vs. 80-85 percent earlier) would give a higher accumulated concentration of the extra sulfur species. Higher chloride concentrations in the earlier tests (as high as 10,000 ppm vs. about 2000 ppm in the later tests) would have a tendency to mask the existence of the extra sulfur species in the ionic balance.

Section 30

CHEMICAL ANALYSIS OF VARIOUS LIMESTONES

As part of a separate EPA Limestone Type and Grind Program, various limestones from the continental United States have been analyzed for their chemical composition. The program has been temporarily suspended with the termination of the Shawnee Program. However, the results of chemical analysis of 138 limestone samples are presented here for the interested readers.

With the cooperation of the National Crushed Stone Association and the National Limestone Institute, 138 limestone samples weighing 25 pounds each were received from various producers located mainly in the eastern and mid-western United States.

All samples were ground and analyzed at the Bechtel Slurry Laboratory (designated as "Lab" in Table 30-1) in San Francisco. Each sample was dried and analyzed for acid insolubles (AI), calcium, magnesium, and carbonate content. Procedures were taken from the Standard Methods for the Examination of Water and Wastewater, 14th Edition.

In support of the analyses of the Bechtel Slurry Laboratory, an atomic absorption spectrophotometer (Perkin-Elmer, Model 403) was used at the Shawnee laboratory (designated as "Shawnee" in Table 30-1) to determine the calcium and magnesium content of each sample. The results of both analyses are given in Table 30.1.

Table 30-1

RESULTS OF CHEMICAL ANALYSES OF LIMESTONE SAMPLES IN WEIGHT PERCENT

Sample Number	Shawnee Ca^{++}	Lab Ca^{++}	Shawnee Mg^{++}	Lab Mg^{++}	Lab $CO_3^{=}$	Lab Al	Lab Total	Location	Company	Contact
001	33.14	33.30	1.33	1.89	52.37	11.42	98.98		Frazier Quarry Inc. P.O. Box 695, Harrisburg, VA 22801	
002	33.71	34.50	1.87	1.82	52.94	8.41	97.67	Clarksville, TN	Vulcan Materials Company, P.O. Box 7497, Birmingham, AL 35223	Don Powell - (205) 877-3211
003	33.79	37.00	1.75	0.61	55.30	6.51	99.42	River Road Plant, Nashville, TN	"	"
004	37.57	38.50	0.36	0.24	58.47	2.56	99.77	Prairie Du Roche, IL	Columbia Quarry P.O. Box 121, Columbia, IL	"
005	35.57	32.50	1.75	3.96	56.44	4.93	97.83	Ullin, IL	"	"
006	39.29	38.90	0.66	0.61	58.99	0.11	98.61	Valmeyer, IL	"	"
007	35.00	35.75	1.81	1.72	55.46	5.66	98.59	Dupo, IL	"	"
008	33.00	33.00	1.81	3.72	51.35	9.66	97.73	White Hill, IL	"	"
009	35.00	34.00	2.05	2.74	55.93	5.75	98.42	Columbia, IL	"	"
010	36.29	37.50	1.15	0.35	54.45	5.81	98.11		Bloomington Crushed Stone Co., Inc. Daval Road, P.O. Box 849 Bloomington, IN 47402	
011	39.29	40.00	0.18	0.00	60.00	0.10	100.10	Fort Dodge, IA	McCarten, Inc. 522 So. 22nd St., Fort Dodge, IA 50501	McCarten - (515) 573-8151
012	39.79	39.20	0.18	0.18	60.50	0.31	100.19	Fort Dodge, IA	"	"
013	37.36	39.00	1.15	0.91	57.98	1.77	99.66		Limestone Products Corp. of America P.O. Box 490, Newton, NJ 07860	
014	34.07	34.70	3.92	3.90	58.48	1.32	98.40		"	
015	32.36	32.00	1.93	1.83	52.17	12.74	98.74		"	
016	39.29	38.70	0.30	0.79	58.99	0.40	98.88		Calcium Carbonate Company Front & Eighth Street, Quincy, IL	
017	33.79	38.50	4.22	1.22	57.98	1.76	99.46	Calera Plant Calera, AL	Vulcan Materials Company P.O. Box 7497, Birmingham, AL 35223	Don Powell - (205) 877-3211
018	38.36	33.50	2.05	2.44	54.78	8.13	98.85	Russelville, AL	"	"
019	37.29	35.00	1.75	2.01	54.96	5.39	97.36	Scottsboro, AL	"	"
020	35.50	35.20	1.15	1.16	53.44	9.94	99.74	Benton County Holladay, TN	Vulcan Materials Company P.O. Box 7497, Birmingham, AL 35223	Don Powell - (205) 877-3211
021	35.43	35.50	0.18	0.48	54.95	10.25	101.18	Huebner Quarry San Antonio, TX	"	"
022	33.57	33.50	1.57	1.83	54.78	9.18	99.29	Parsons, TN	"	"
023	36.50	35.50	0.66	1.52	55.46	5.97	98.45	Tuscumbia Quarry Tuscumbia, AL	"	"
024	36.21	35.00	1.27	1.46	54.40	7.13	97.99	Huntsville, AL	"	"
025	37.71	39.00	1.15	0.91	56.97	3.14	100.02	Glenco Plant Glenco, AL	"	"
026	35.29	35.30	2.11	2.07	59.24	4.37	100.98	Wolf Creek, KY	Owensboro River Sand & Gravel Co., Inc. P.O. Box 1538, Owensboro, KY 42301	John A. Yager - (502) 926-3611
027	35.64	36.40	4.10	0.70	53.94	6.71	97.75	Hillsboro, OH	Highland Stone Division of Davon, Inc. 4281 Roush Rd., Hillsboro, OH 45133	J. Craig Morgan - (513) 393-4211
028	38.29	38.00	0.24	0.48	58.99	2.48	99.95	South Quarry Rapid City, SD	Pete Lien & Sons, Inc. P.O. Box 440, Rapid City, SD 57709	C. H. Lien - (605) 342-7224
029	36.57	35.00	0.60	1.22	54.95	9.04	100.21	Greenbriar Limestone at Elkins, WV	J. F. Allen Company P.O. Box 49, Clarksburg, WV 26301	David G. Allen - (304) 623-3336
030										
031	37.36	38.00	1.03	0.61	56.97	4.16	99.74	Pringle Quarry Rapid City, SD	Pete Lien & Sons, Inc. P.O. Box 440, Rapid City, SD 57709	C. H. Lien - (605) 342-7224 Sam Frederick
032	38.21	38.90	1.39	0.73	59.49	1.01	100.13	Gulliver, MI	Inland Lime & Stone Co. Gulliver, MI 49840	A. J. Cayia - (906) 283-2615
033	28.79	29.00	3.62	3.35	49.91	15.52	97.78	Kickapoo Stone U.S. 24, Peru, IN	Rock Industries, Inc. P.O. Box 112, Peru, IN 46970	Terry W. Smith - (317) 473-5578 Robert Koehler
034	39.07	39.50	0.30	0.30	58.99	0.53	99.32	Jonesboro, IL	American Limestone Co. P.O. Box 2389, Knoxville, TN 37901	Hoy L. Gill - (615) 573-4501
035	37.79	38.00	0.96	0.85	58.43	1.77	99.05		Black River Mining P.O. Box 1, Butler, KY 41006	

Table 30-1 (continued)

RESULTS OF CHEMICAL ANALYSES OF LIMESTONE SAMPLES IN WEIGHT PERCENT

Sample Number	Shawnee Ca^{++}	Lab Ca^{++}	Shawnee Mg^{++}	Lab Mg^{++}	Lab $CO_3^{=}$	Lab Al	Lab Total	Location	Company	Contact
036	32.86	33.00	3.56	2.74	60.00	5.41	101.17	Branford, FL	Hatch Enterprises, Inc. P.O. Box 238, Branford, FL 32002	Rudolph Hatch - (904) 935-1419
037	33.00	32.00	0.54	1.52	47.39	15.04	95.95	Chico, TX	General Portland, Inc. P.O. Box 324, Dallas, TX 75221	Tom Schneider - (214) 387-4700
038	38.93	40.10	0.48	0.12	60.00	1.10	101.32	-	-	-
039	25.86	24.80	0.42	0.84	46.89	34.40	106.93	Cheek Towaye Quarry Buffalo, NY	Buffalo Slag Co., Inc. 111 Great Arrow Ave. Buffalo, NY 14216	Gary D. Nelson - (716) 683-4714
040	37.36	38.30	1.03	0.61	58.99	2.43	100.33	Millard Quarry Annville, PA 17003	Bethlehem Mines Corp. Stone & Slag Div. Bethlehem, PA 18016	E. V. Leedecker - (215) 694-4841
041	20.64	22.50	9.17	8.54	52.17	14.74	97.95	Talmage Quarry Talmage, PA	D. M. Stolzfus & Son, Inc. Talmage, PA 17580	M. A. Stoltzfus - (717) 656-2411
042	37.57	38.40	0.66	0.24	56.97	2.52	98.13	Chico TX	General Portland, Inc. P.O. Box 324, Dallas, TX 75221	Tom Schneider - (214) 387-4700
043	35.79	36.00	1.81	1.83	57.39	2.91	98.13		East St. Louis Stone Co. 7705 West Main St. Belleville, IL 62223	E. A. McLeon - (618) 271-0610
044	37.14	37.00	0.30	0.91	56.97	4.56	99.44	Lowellville, OH	The Carbon Limestone Co. Lowellville, OH 44436	W. S. Foster - (216) 536-6275
045	28.50	28.80	1.51	1.46	49.91	22.16	102.33		County Line Stone Co., Inc. County Line Rd. Akron, NY 14001	J. W. Buyers - (716) 542-5435
046	38.71	39.00	0.42	0.30	58.48	2.01	99.79	Berkeley Quarry Southeast Div., Rte 1, Box 147 Cross, SC 29436	Martin Marietta Aggregates 6801 Rockledge Dr. Bethesda, MD 20034	Dr. Frank Ozol - (301) 247-0700 Ext: 414
047	38.21	39.00	0.18	0.00	58.99	2.63	100.62	Indianapolis Quarry Central Div., P.O. Box 50815 Indianapolis, IN 46250	-	-
048	35.93	37.50	1.03	0.91	57.47	4.47	100.35	Jamesville Quarry P.O. Box 390, Road Cut Rd., Jamesville, NY 13078	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	Fred C. Moore - (215) 253-4217
049	37.79	36.70	0.78	1.22	60.00	2.24	100.16	Midway Quarry Knoxville,TN	American Limestone Co. P.O. Box 2389, Knoxville, TN 37901	Hoyl Gill - (615) 573-4501
050	38.86	38.50	0.78	0.31	58.99	0.18	97.98	Forks of the River Quarry Knoxville, TN	-	-
051	39.07	39.10	0.30	0.24	58.99	2.04	100.37	Middletown Quarry	Flintkote Stone Products Co. Executive Plaza IV 11350 McCormick Rd. Hunt Valley, MD 21031	John A. West - (301) 628-4000
052	35.93	34.00	1.03	3.66	56.97	2.94	97.57	Medford Quarry	Flintkote Stone Products Co. Executive Plaza IV 11350 McCormick Rd. Hunt Valley, MD 21031	John A. West - (301) 628-4000
053	29.71	30.50	1.21	0.91	45.37	21.60	98.38	Frederick Quarry	-	-
054	32.93	31.00	1.57	1.89	51.35	16.54	100.78	Skaneateles Quarry P.O. Box 86, Rte. 321 Skaneateles, NY 13152	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	Carl Currier
055	33.14	32.50	1.15	1.40	52.94	12.92	99.76	Rossville Quarry TN	Stone Man Inc. P.O. Box 2098, 3908-B Tennessee Ave. Chattanooga, TN 37409	Don Connell - (615) 821-7533
056	38.43	37.50	1.03	1.22	57.45	2.91	99.08	Murfreesburo Quarry TN	-	-
057	38.00	37.50	1.15	0.79	56.50	4.35	99.14	Shelbyville Quarry TN	-	-
058	26.50	27.00	0.90	4.57	45.37	27.07	104.01	Honeoye Falls Quarry P.O. Box 151, NY 14472	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	Bennett Gardiner
059	37.71	38.30	1.09	0.98	58.48	1.48	99.24	McMinnville Quarry TN	Stone Man Inc. P.O. Box 2098, 3908-B Tennessee Ave. Chattanooga, TN 37409	Don Connell - (615) 821-7533
060	37.57	36.90	0.60	1.00	54.45	5.68	98.03	Tiftonia Quarry TN	-	-
061	36.71	36.50	0.66	0.90	54.56	6.02	97.98	Watertown Quarry P.O. Box 130 Watertown, NY 13601	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	Fred C. Moore - (215) 253-4217
062	23.93	26.00	6.81	5.49	51.35	16.53	99.37	Blue Ridge, VA	Blue Ridge Stone Corp. P.O.Box 13527 Roanoke, VA 24035	Robert McMinnis
063	36.64	36.50	0.96	0.90	55.96	4.34	97.70	Bluefield, VA	Pounding Mill Quarry Corp. P.O. Box 13527 Roanoke, VA 24035	-
064	35.93	36.50	1.15	1.89	56.47	6.16	101.02	Bluefield, VA	-	-
065	31.14	31.10	1.39	1.50	51.58	16.28	100.46	Pounding Mill, VA	-	-
066	38.29	39.00	0.12	0.37	57.93	0.76	98.06	Montour Quarry Tama, IA	B. L. Anderson Inc. 327 Guaranty Blvd. Cedar Rapids, IA 52401	Dow E. Prouty - (319) 363-8131
067	29.29	30.90	6.45	5.40	58.99	3.78	99.07	Garrison Quarry Vinton, IA	-	-

Table 30-1 (continued)

RESULTS OF CHEMICAL ANALYSES OF LIMESTONE SAMPLES IN WEIGHT PERCENT

Sample Number	Shawnee Ca^{++}	Lab Ca^{++}	Shawnee Mg^{++}	Lab Mg^{++}	Lab CO$_3^{=}$	Lab Al	Lab Total	Location	Company	Contact
068	21.57	22.80	12.84	12.26	62.03	2.49	99.58	Sodus Quarry 7211 Quarry Rd. Sodus, NY 14551	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	R. T. Parton
069	38.21	39.50	0.36	0.30	56.97	2.59	99.36		Lime Products Corp. Box 357, Union, ME 04862	R. A. Kaler - (207) 785-2266
070	38.36	37.90	0.24	0.30	57.22	4.52	99.94	Defiance Quarry Defiance, MO	St. Charles Quarry Co.	W. W. Sanders, Jr. - (314) 724-3641
071	38.14	39.10	0.18	0.12	57.96	2.39	99.57	Albany Quarry P.O. Box 637 Leesburg, GA 31763	Martin Marietta Aggregates 6801 Rockledge Dr. Bethesda, MY 20034	Dr. Frank Ozol - (301) 247-0700 Xt: 414 G. Brown - (912) 759-6435
072	21.14	24.04	12.60	11.89	62.08	0.49	98.50		J. E. Baker Co. P.O. Box 1189 York, PA 17405	P. F. Hummer - (717) 848-1501
073	36.14	36.80	1.09	0.73	56.95	5.21	99.69	Festus Plant Jefferson County, MO	Fred Weber, Inc. Materials Div., 7929 Alabama Ave. St. Louis, MO 63111	William Powell - (314) 739-6050
074	25.71	26.50	3.98	4.27	51.50	19.14	101.41	Geneva Plant Pre-Emption Rd., County Rd. 6 Oaks Corners, NY 14518	General Crushed Stone Co. P.O. Box 231 Easton, PA 18042	Charles T. Carroll
075	36.29	36.50	0.84	1.52	53.94	6.71	98.67	North Plant St. Louis, MO	Fred Weber, Inc. Materials Div., 7929 Alabama Ave. St. Louis, MO 63111	William Powell - (314) 739-6050
076	23.29	22.80	1.09	1.10	39.83	37.93	101.66	Dufferin Quarry Hagersville, Ontario	Dufferin Aggregates 3625 Dufferin St. Downsview, Ontario M3K1N5	J. Sutherland - 630-4422
077	19.64	22.00	13.14	12.00	62.08	0.86	96.94	Dufferin Quarry Milton, Ontario	"	"
078	28.43	28.70	1.15	0.79	50.92	22.21	102.62	Wallace Stone Plant Bay Port, MI	J. P. Burroughs & Son, Inc. 8785 Ribble Rd Bay Port, MI 48720	James Reid - (517) 656-2831
079	34.07	34.00	1.03	1.22	52.43	10.71	98.36	Richards Spur Quarry Elgin, OK	Dolese Bros. Co. 20 NW 13th St. Oklahoma City, OK 73101	A. Darrell George - (405) 235-2311
080	36.93	36.20	1.69	2.28	[illegible].99	2.18	99.65	Konawa Quarry Konawa, OK	"	"
081	33.14	35.00	1.99	1.40	54.96	8.92	100.28	Big Canyon Quarry Sulphur, OK	"	"
082	32.93	33.10	1.57	1.77	49.91	10.74	105.52		Luck Quarries, Inc. P.O. Box 29682 Richmond, VA 23229	Charles S. Luck - (804) 784-3335 M. F. Rothweiler, Jr. (804) 749-3615
083	24.21	26.50	9.89	8.26	58.99	4.54	98.26	Millard Quarry Annville, PA 17003	Blackstone Mines Inc. Annville, PA 17003	E. K. Leedecker
084	21.14	21.50	11.82	12.20	61.00	5.53	100.23	Findlay Quarry OH	National Lime and Stone Co. First National Bank Bldg. Findlay, OH 45840	James Welshimer - (419) 396-7671
085	21.79	21.00	10.25	11.89	59.70	5.63	98.22	Carey C-3 Quarry OH	"	"
086	36.00	35.30	2.77	2.40	58.40	3.19	99.29	Delaware Quarry OH	"	"
087	33.00	31.90	4.70	4.10	58.90	3.34	98.24	Bucyrus Quarry OH	"	"
088	22.14	22.50	12.54	11.89	62.60	1.55	98.54	Carey C-4 Quarry OH	"	"
089	20.07	21.00	12.42	12.81	61.50	4.39	99.70	Bucyrus Quarry OH	"	"
090	21.43	22.50	12.60	12.00	60.00	3.85	98.35	Rimer Quarry OH	"	"
091	21.71	22.00	13.75	12.50	64.69	0.17	99.36	Carey C-2 Quarry OH	"	"
092	27.21	28.50	6.81	6.16	57.40	6.69	98.75	Marion Quarry OH	"	"
093	20.43	20.70	11.94	11.50	59.23	7.50	98.93	Lima Quarry OH	"	"
094	27.71	29.50	6.57	5.90	58.00	6.80	100.20	Marion Quarry OH	"	"
095	22.14	22.30	12.30	12.30	63.13	0.51	98.24	Carey C-1 Quarry OH	"	"
096	21.43	22.50	13.81	12.80	64.06	0.88	100.24	Buckland Quarry OH	"	"

Table 30-1 (continued)

RESULTS OF CHEMICAL ANALYSES OF LIMESTONE SAMPLES IN WEIGHT PERCENT

Sample Number	Shawnee Ca^{++}	Lab Ca^{++}	Shawnee Mg^{++}	Lab Mg^{++}	Lab $CO_3^{=}$	Lab Al	Lab Total	Location	Company	Contact
097	39.43	37.00	0.30	0.80	60.50	0.93	99.23		Franklin Limestone Co 612 Tenth Ave., N. Nashville, TN 37203	(615) 259-4222
098	39.71	38.75	0.42	0.45	60.00	0.77	99.97		Southern Stone Co. (Longview Limestone Co.) P.O. Box 38 Saginaw, AL 35137	
099	37.36	38.40	0.66	0.61	57.90	4.46	101.37	Quarry #6 Montgomery County, KS	Midwest Minerals, Inc. P.O. Box 412 Pittsburg, KS 66762	R. A. Atkinson - (316) 231-8120
100	39.50	38.50	0.30	0.70	59.60	1.10	99.90	Quarry # 15 Benton County, MO	"	"
101	35.79	36.50	1.03	1.22	58.50	3.81	100.03	Edgerton Quarry, Kansas Spring Hill Ledge	Martin Marietta Aggregates 6801 Rockledge Dr. Bethesda, MD 20034	Dr. Frank Ozol - (301) 247-0700 Xt: 414 Chas. W. Nichols, 1305 W. 42nd St. Topeka, KS 66604 (913) 266-5556
102	36.93	35.00	1.27	0.00	58.00	5.08	98.08	E. Topeka Quarry, Kansas Ervine Creek Ledge	"	"
103	38.43	38.50	0.72	0.61	59.00	1.97	100.08	Moline Quarry, Kansas Ervine Creek Ledge	"	"
104	37.43	37.80	0.48	0.24	58.50	2.60	99.14	Ottawa Quarry, Kansas Stoner Ledge	"	"
105	36.07	35.90	1.09	1.58	57.70	4.79	99.97	Lansing Quarry, Kansas Captain Creek Ledge	"	"
106	33.93	35.50	1.87	1.60	57.50	6.44	101.04	Lansing Quarry, Kansas Spring Hill Ledge	"	"
107	36.86	35.50	1.15	1.20	56.90	5.00	98.60	Ottawa Quarry, Kansas Captain Creek Ledge	"	"
108	38.43	35.50	0.48	0.30	60.00	3.06	98.86	Edgerton Quarry, Kansas Stoner Ledge	"	"
109	38.43	38.00	0.54	0.80	59.50	2.13	100.43	Edgerton Quarry, Kansas Captain Creek Ledge	"	"
110	30.93	31.00	3.74	5.49	58.50	3.85	98.84	E. Topeka Quarry, Kansas Ozawkie Ledge	"	"
111	33.36	31.00	2.77	2.44	56.90	4.37	94.71	Lansing Quarry, Kansas Stoner Ledge	"	"
112	39.29	37.20	0.36	0.90	56.90	4.59	99.59	Ewing Plant Lewis County, MO	Missouri Gravel Co.	Bob Savage - (309) 762-5541 Howard Art Dixon - (309) 757-8250 Moline Consumers Co.
113	39.71	38.00	0.24	0.70	58.90	2.16	99.76	Huntington Plant Rolls County, MO	Central Stone Company RR #1, Hannibal, MO 63401	"
114	36.50	37.00	1.03	0.92	58.50	4.48	100.90	Bethel Plant Sholby, MO	"	"
115	37.71	37.50	0.12	0.18	56.40	4.56	98.64	Allied Quarry Milan, IL	Allied Stone Co.	"
116	37.14	35.90	1.45	2.00	58.20	3.18	99.28	Elkton, KY	Kentucky Stone Co. P.O. Box 7556, Louisville, KY 40207	Broadus N. Davidson - (502) 897-1731
117	33.43	33.50	0.90	1.65	55.00	11.78	101.93	Canton, KY	"	"
118	35.64	36.00	2.17	2.60	59.00	3.13	100.73	Franklin, KY	"	"
119	32.93	33.00	3.62	3.96	56.97	5.97	99.90	Irvington, KY	"	"
120	38.71	38.00	0.66	1.22	60.00	1.42	100.64	Irvington, KY	"	"
121	37.79	37.50	0.78	0.61	58.50	2.51	99.12	Upton, KY	"	"
122	37.00	37.80	1.33	0.73	58.50	2.39	99.42	Princeton, KY	"	"
123	38.43	37.00	1.15	1.00	58.00	2.40	98.40	Russellville, KY	"	"
124	36.50	35.30	0.60	1.40	56.50	6.56	99.76	Marion, KY	"	"
125	36.21	36.50	1.21	0.92	56.00	4.97	98.38	Princeton, KY	"	"
126	36.29	37.00	0.54	0.50	58.50	3.31	99.31	Snowflake, WV	Acme Limestone Co. P.O. Box 27 Fort Spring, WV 24936	Rodney H. Peck - (304) 647-4443
127	31.07	29.30	1.21	1.50	46.52	20.50	97.82	Snowflake, WV	"	"
128	25.93	25.00	4.58	4.58	50.70	17.10	97.37	Carthage Quarry Carthage, IL	Colchester Stone Co.	Bob Savage - (309) 762-5541 Howard Art Dixon - (309) 757-8250 Moline Consumers Co.
129	30.79	30.00	2.05	2.50	52.62	15.38	100.50	Valley Quarry St. Augustine, IL	Moline Consumers Co. 313 16th St., Moline, IL 61265	"
130	34.57	32.70	3.20	3.10	58.69	4.60	99.09	Colchester Quarry Colchester, IL	Colchester Stone Co.	"
131	39.00	39.00	0.36	0.35	59.85	0.57	99.76	Nashville, TN	Calcium Products Division of Cowen Stone Co. 480 Craighead St., Suite 201 Nashville, TN 37204	W. H. Summers - (615) 297-6579
132	38.43	39.00	0.24	0.61	60.00	0.83	100.44	Indiana Cal-Pro, Inc. 480 Craighead St., Suite 201 Nashville, TN	"	"

Table 30-1 (continued)

RESULTS OF CHEMICAL ANALYSIS OF LIMESTONE SAMPLES IN WEIGHT PERCENT

Sample Number	Shawnee Ca^{++}	Lab Ca^{++}	Shawnee Mg^{++}	Lab Mg^{++}	Lab $CO_3^{=}$	Lab Al	Lab Total	Location	Company	Contact
133	37.50	38.00	0.25	0.48	57.50	3.63	99.61	Harris West Boundry	Granite Rock Co. Watsonville, CA	
134	34.35	36.80	0.10	0.43	55.00	7.10	99.33	Monterey Coast (Pico Blanco)	Granite Rock Co. Watsonville, CA	
135	32.20	35.00	0.56	0.30	53.00	12.49	100.79	White Rock Quarry	Martin Marietta Aggregate, Centre Co., PA	
136	35.95	38.60	0.41	0.85	57.98	1.10	98.53	Pinesburry Quarry	Martin Marietta Aggregate Williamsport, MD	
137	36.85	38.20	0.37	0.91	57.73	2.04	98.88	Power Screen Fines	Warren Co. Bell-Mine Lime-L/S Products Bellefont, PA	
138	40.52	-	0.22	-	-	-	-	Ste. Genevieve, MO	Mississippi Lime Co. Alton, IL 62002	Jack Raierlein (618) 465-7741

Section 31

EQUIPMENT OPERATING EXPERIENCE AND MATERIALS TESTING

This section summarizes equipment operating experience during the reporting period with Shawnee lime and limestone scrubber systems operating with both high and low fly ash loading in the flue gas, with and without adipic acid addition, and with and without forced oxidation.

31.1 SCRUBBER INTERNALS

31.1.1 Mist Eliminators

The reliability of the mist elimination system was studied extensively from March 1972 to early 1976 (Reference 6). As a result of that study, a mist eliminator of an open vane, three pass, 316L stainless steel chevron design was chosen for all subsequent tests. The perpendicular clearance between parallel blades was 2-1/2 inches. The wash requirements are shown in Table 31-1.

During this test period, the mist eliminator operated reliably and free of pluggage. Deposits contributing to more than 2 or 3 percent restriction have occurred on only a few occasions. The mist eliminator underspray nozzles have operated satisfactorily using a mixture of clarified process water and river water (makeup water). On approximately three occasions the underspray nozzles were cleaned of slurry solids that carried over from the clarifier.

In early May 1979, a new mist eliminator made of 10 gauge stainless steel was installed in the TCA. The design was identical to the previous mist eliminator

Table 31-1

MIST ELIMINATOR WASH SYSTEMS

Alkali	LIME SCRUBBING		LIMESTONE SCRUBBING	
Scrubber System	Spray Tower(4)	TCA	Spray Tower(4)	TCA
Maximum Flue gas rate, acfm @ 300°F	35,000	30,000	35,000	30,000
Bottomside M.E. Wash				
Wash scheme	Low Intermittent	Low Intermittent	Continuous	Continuous
Nozzle size and model(1)	1/2 G35W	1-1/4 H190WSQ	1/2 G35W	3/4 HH71WSQ
Number of nozzles	10	2	4	2
Nozzle location, inches below M.E.	10	31	20	31
Nozzle "on" time, min	6	6	Continuous	Continuous
Nozzle "off" time, min	234	234	-	-
Total on/off sequence, hr	4	4	-	-
Nozzle ΔP, psi	50	41	21	20
Flow rate per nozzle, gpm	7.5	37.5	5.0	10
Total flow rate, gpm	75	75	20(3)	20(3)
Specific wash rate, gpm/ft^2	1.5	1.5	0.4	0.4
Makeup water (continuous basis), gpm	1.9	1.9	20(3)	20(3)
Topside M.E. Wash				
Wash Scheme	Low Intermittent	Low Intermittent	High Intermittent	High Intermittent
Nozzle size and model(1)	3/4 H6W	3/4 HH71WSQ	3/4 H6W	3/4 HH71WSQ
Number of nozzles	6	6	6	6
Nozzle location, inches above M.E.	16	15	16	15
Nozzle "on" time, min(2)	4	4	3	3
Nozzle "off" time, min	76	76	7	7
Total on/off sequence, min	80	80	10	10
Nozzle ΔP, psi	13	13	13	13
Coverage area per nozzle, ft^2	15	14.5	15	14.5
Flow rate per nozzle, gpm	8	8	8	8
Specific wash rate, gpm/ft^2	0.53	0.55	0.53	0.55
Makeup water (continuous basis), gpm	0.4	0.4	2.4	2.4

Notes:
(1) All nozzles are full cone type manufactured by Spraying Systems Co.
(2) Sequential wash with one nozzle activated at a time.
(3) Clarified liquor from dewatering system diluted with makeup water; at 20,000 acfm gas rate, underwash is 15 gpm.
(4) Spray tower includes venturi/spray tower system.

except that the old mist eliminator blades were made of 16 gauge stainless steel that had deformed over the years from the weight of workmen.

On September 25, 1979, a new mist eliminator was installed in the venturi/spray tower for similar reasons with design considerations similar to those for the TCA.

31.1.2 TCA Grid Supports

The 3/8-inch diameter, Type 316L stainless steel bars, installed at 1-1/4 inch centers, were in slurry service for approximately 7-1/2 years with no evidence of significant erosion. Other than the mistaken installation of a few non-316L stainless steel pieces, the bars have operated trouble-free and have supported both mobile spheres and fixed packing.

31.1.3 TCA Spheres

For this test period three lots of nitrile foam spheres were used. Before this test period, 6.5-gram (1-1/2 inch diameter) UOP nitrile foam spheres were tested. The 6.5-gram spheres performed well, did not fail structurally, but did wear gradually until they became small enough to migrate through the TCA grid bars. On July 3, 1978, larger 11.5-gram (1-7/8 inch diameter) UOP nitrile foam spheres were installed (lot #1098). On August 4, 1978, lot #1098, which was failing due to a manufacturing defect, was replaced with lot #1101. The defect was the high percentage of open pores in the spheres which resulted in significant weight gain during testing. Lot #1101 was also 1-7/8 inches in diameter. The lot #1101 spheres were monitored for size and weight change for eight months. The results are listed in Table 31-2.

Table 31-2

NITRILE FOAM SPHERE WEIGHT AND DIAMETER CHANGE

(Lot 1101)

Date	Duration (days)	Weight (gm)	Diameter (in.)
08/04/78 (new)	0	11.55	1.89
09/06/78	33	12.29	----
09/13/78	40	13.27	----
09/20/78	47	13.78	1.72
10/02/78	59	13.19	1.71
10/20/78	77	13.24	1.77
11/02/78	90	12.20	1.78
11/27/78	115	12.04	1.68
01/25/79	174	12.22	1.54
02/08/79	188	12.10	1.59
03/15/79	223	11.40	1.57
04/06/79	245	10.75	1.50

On April 6, 1979, lot #1101 spheres had worn to such an extent that the original bed depth of 5 inches per bed for 3 beds became 4-1/2 inches (top), 4 inches (middle) and 4-1/4 inches (bottom). Although the lot #1101 spheres were performing satisfactorily, they were replaced with similar new spheres (lot #1199) in order to establish 5 inches per bed of spheres of uniform service life. The lot #1101 spheres were later used as makeup spheres.

On July 15, 1980, new 6-gram (1-1/2 inch diameter) high density polyethylene (HDPE) spheres obtained from Puget Sound Trading Company were installed in the TCA in support of the Springfield City Utilities Full-Scale TCA Simulation Program (see Section 20). On September 10, 1980, after 1240 hours of service, the spheres were inspected and showed severe splitting and cracking. Sphere failure per bed ranged between 35 and 50 percent; the manufacturer speculated that the problem was a defect in the manufacturing technique. The failed spheres were partly replaced with about 10,500 new ones on September 10. All spheres were subsequently replaced with a new batch on September 22. After 1216 hours of service, the new batch of HDPE spheres was inspected and showed approximately 10, 5, and 1 percent failure in the top, middle, and bottom beds, respectively. The spheres were removed on November 17, 1980, and fixed packing was installed.

31.1.4 TCA Fixed Packing

On November 24, 1980, 4 ft (23 layers) of Glitsch Grid fixed packing (Type 2Z 316L stainless steel, fabricated by Glitsch, Inc.) was installed in the TCA (see Section 21). Due to higher than expected pressure drop, the packing was reduced from 23 layers to 12 and then to 7 layers. Serious scaling occurred on the grid surfaces in 235 hours of service without cleaning. Erosion and corrosion were not observed during this period.

31.1.5 TCA Nozzles

The four main slurry spray nozzles in the TCA were Model 1969F full-cone, open type nozzles, manufactured of Type 316L stainless steel by Spraco. During 7-1/2 years in service, the nozzles provided excellent service both in terms of wear and non-clogging characteristics. Over the years, only minor erosion occurred at the discharge orifice and was attributed to the low pressure drop (about 5 psi) across the nozzles.

The three inlet gas cooling spray nozzles were Bete No. ST32FCN (full cone) with Stellite diffusers (spiral tip). The nozzles effectively used slurry to cool the scrubber inlet flue gas, and because strainers were present the nozzles seldom plugged.

31.1.6 Venturi/Presaturator

The venturi/spray tower combined system continued to be operated from the beginning of this report period to the end of May 1980. During this period erosion of the 316L stainless steel venturi persisted in selected areas, most notably the four guide vanes on the plug support shaft and the outer walls. The vanes were repeatedly patched and resurfaced. In early October 1978 the plug support shaft and guide vanes were replaced, and new Rulon guide blocks and block supports were installed. By May 1980 the top surfaces of the 316L stainless steel vanes were again severely eroded, as much as 2 inches at some locations. The venturi walls were patched at six locations with 316L stainless steel plate. In July 1978, the plug drive limit switch was replaced twice, and in March 1980, the plug drive motor failed.

Interest in the spray tower testing prompted the decision in June 1980 to remove the venturi section and replace it with a conventional presaturator section.

The presaturator was similar in design to that located in the inlet duct of the TCA. The material of construction was 316L stainless steel. Epoxylite 203 was applied on the junction between the presaturator and the spray tower neoprene lining. An air soot blower (Copes-Vulcan T-30MK-IE) was installed to blow off accumulated soft solids at the wet/dry interface at a frequency of three times per day. The soot blower operated trouble-free and effectively.

31.1.7 Spray Tower Trap-out Funnel

Separation of slurry leaving the venturi scrubber from that leaving the spray tower was desireable to achieve two independent scrubber loops for forced oxidation testing. This flow separation was accomplished by installing a large trap-out funnel in the spray tower below the bottom spray header (see Figure 4-1). Note that a trap-out funnel would not necessarily be practical for slurry service because of its potential fouling problem, but it was expedient at Shawnee. No evidence of corrosion was observed on the funnel, which was constructed of 316L stainless steel. During normal operation, accumulations of solids on the underside (gas side) of the funnel were a common occurrence. In October 1979, the trap-out funnel was removed and single loop testing commenced.

31.1.8 Venturi/Spray Tower Nozzles and Headers

The spray tower slurry nozzles were Bete No. ST48FCN, all Stellite (orginally manufactured as 316L stainless steel base with Stellite diffuser). The nozzles were normally operated at 10 to 15 psi pressure drop. Plugging occurred intermittently depending on scrubber operating conditions and the condition of the slurry strainers located upstream of the nozzles.

The original four spray tower slurry headers (spaced 4 ft apart) consisted of 7 nozzles each. In August 1980 the existing 4-inch diameter headers were replaced with four larger capacity 6-inch diameter headers of 316L stainless steel. Each 6-inch header had 12 nozzles. The flow capacity for the old and new headers was 400 gpm and 600 gpm, respectively. The venturi scrubber contained four tangential nozzles and one bull nozzle made of open-ended pipes. Both types of nozzles worked effectively in slurry service and only infrequent plugging of the tangential nozzles occurred. The tangential nozzles had a Y-strainer upstream.

The presaturator contained three Bete No. ST32FCN Stellite nozzles, one located on each side wall and one on top. Slurry was used for presaturation of the flue gas. Plugging was minimal and resulted when loose scale solids passed through malfunctioning Y-strainers located upstream of the nozzles.

31.2 OXIDIZERS

The slurry oxidation system consisted of an air sparger located at the bottom of the oxidation tank, a slurry agitator, and air compressor/blower.

31.2.1 Air Spargers

Venturi/Spray Tower. The oxidation tank on the venturi/spray tower system was 8 ft in diameter and 20 ft high and was made of epoxy coated carbon steel. During the first part of this test period air was introduced via a 3-inch diameter open pipe 6 inches above the tank floor pointing downward.

During single tank, forced oxidation tests, severe pump cavitation problems were encountered due to entrained air bubbles in the pump suction. The problem was solved by relocating the air discharge point to an elevation 45 inches above the tank floor and discharging the air upward. Additionally, baffle plates were installed in the tank near the pump suction opening in order to "shelter" the pump from air bubbles. These modifications proved successful (Figure 9-2).

TCA. The TCA air sparger during the Springfield simulation tests was a five prong assembly of 3 and 4 inch diameter 316L stainless steel pipe sections. On the underside of the pipe sections were 40 holes spaced approximately two ft apart. Each hole consisted of a 1/4-inch diameter by 3/4-inch long nipple welded onto the header. The oxidation tank was a 20 ft diameter Flakeline-lined carbon steel tank that was normally operated at a liquid level between 11 and 18 ft.

The TCA sparger assembly operated with qualified success. Complete oxidation was obtainable but after approximately five weeks of operation the header filled with slurry solids to such a degree that air flow could not be maintained. Attempts at high pressure air/water flushing were unsuccessful. Upon inspection, the header was approximately half full of solids overall, i.e., open at the air entry end, 1/4 full of solids half way through the pipe, and totally full the last 1/3 of the pipe.

A 7-ft diameter, 21-ft high oxidation tank was also used on the TCA system with a 3-inch diameter open pipe as an air sparger. Air was discharged downward 5 inches from the tank bottom. This system operated effectively, without problems.

31.2.2 Compressor/Blower

A Worthington type VBB, size 14-1/2 x 9 inch, single cylinder air compressor with 100 Hp motor was used for both the venturi/spray tower and TCA systems during the first part of this test period. The compressor was an oil-free, non-lubricating type to avoid possible contamination of slurry by the oxidation inhibitors in the oil.

On March 17, 1979, a second non-lubricating reciprocating compressor was installed. The new 100-Hp Ingersoll-Rand (I-R) compressor was sized at 435 scfm at 80 psig.

The I-R and Worthington compressors were used only as a source of oxidizing air and operated acceptably well. High pressure water flushing of the cooling water jackets to remove river water deposits (mostly mud) was required seven times for both compressors in 33 months. Mechanical problems on the I-R compressor included the failure of the switchgear in April 1979, and the malfunction of the loading/unloading electrical controls in March 1981. The air receiver backpressure regulators were infrequently adjusted or rebuilt and three solenoid valves were replaced on these compressors.

For part of the forced oxidation testing on the TCA in September through November 1980, a 75-Hp rotary lobe blower manufactured by Roots Blower was operated. The blower was rated at 13.5 psig maximum discharge pressure with a capacity of 400 scfm when operated at a reduced pressure of 8-10 psig. This blower was originally used for six months during the DOWA process testing by TVA. While the blower was used for the EPA program, no maintenance was required other than the occasional addition of bearing oil.

31.3 REHEATERS

Scrubbed flue gas was normally reheated to 250°F to prevent acid condensation and corrosion in the exhaust system, to facilitate analytical sampling, to protect the induced-draft fans from solid deposits and droplet erosion, and to increase plume bouyancy.

The original in-line, fuel-oil-fired units supplied by Hauck Mfg. Co. were modified in 1974 and 1975 to incorporate a fuel-oil-fired indirect combustion chamber manufactured by Bloom Engineering Co. The units required moderate maintenance principally on the fuel oil feed system and electrical controls for the ignitor system. The causes were generally attributed to the age and service of the system. The accumulation of dried slurry solids on the walls of the reheater flue gas/hot air mixing chamber periodically occurred. Typically once every three months, accumulations from 1 to 5-inches thick were manually removed.

31.4 INDUCED-DRAFT FANS

The Type 316L stainless steel fans at the Shawnee Test Facility were induced-draft, centrifugal fans manufactured by Zurn Industries. Reliability was fair during this test period, with periodic system downtime due to the following problems:

- Cleaning of the fan, fan dampers, and duct between the dampers and reheaters (approximately fifty times for both systems in 33 months).
- Replacement of the motor or gears on the back damper on eight occasions.

Three events of significance were:

- The TCA Bentley Nevada ID fan vibration sensor unit failed on August 13, 1980, and was shipped back to the manufacturer for repairs. The cocurrent scrubber system (Train 300) vibration sensor instruments were temporarily moved to the TCA to be used until the repairs were completed on the defective unit.
- A new Beck ID fan damper positioner-actuator was installed on the venturi/ spray tower system in September 1980. The new unit was larger (1500 in-lb torque) than the one it replaced (900 in-lb torque) and was installed to help prevent the repetitive maintenance which was required on the smaller unit. The new unit operated satisfactorily.
- On July 9, 1980, a crack was found in the east shroud of the spray tower ID fan extending about 5-3/4 inches from the outer perimeter of the shroud near the weld joining one of the fan blades to the shroud. This crack was in the same location and similar in configuration to the two previously reported cracks which had been repaired (pp. L-20 and L-47, Reference 3, pp. L-23 and L-50, Reference 4). The crack was repaired onsite in August 1980 under the supervision of the manufacturers' representative (Zurn Air System).

31.5 SLURRY PUMPS

31.5.1 Allen-Sherman-Hoff Pumps

The Allen-Sherman-Hoff centrifugal pumps were neoprene lined, slurry service pumps equipped with Nelson liquid Vari-Drive units. The pump packing was conventional graphite-impregnated asbestos. The sleeves were chrome-plated steel. Pump seals were air-flush type used to prevent excess water input to the system.

Considering the wide range of operating conditions experienced, the pumps provided satisfactory service with moderate maintenance. The most frequent maintenance was repacking; the following general trends were believed to be related to repacking frequency.

- Wide flow variation as dictated by changing test conditions
- Operation of a pump at the low-flow end of the pump curve
- The number of pump start/stops

Other routine pump maintenance included fluid change in the Nelson Vari-Drive and replacement of the stuffing box and shaft sleeves.

31.5.2 Moyno Pumps

Moyno pumps are positive displacement, variable speed pumps used primarily for moving thick slurry at Shawnee. Six such pumps were employed as alkali addition pumps. A larger sized Moyno was available for the recirculation of the underflow slurry in the venturi/spray tower clarifier but was seldom used.

Moyno pump rotors are helical shaped and are made of chrome-plated steel for abrasion resistance. Stators are n-butyl rubber-lined with a double helical groove. The most frequent maintenance problem was erosion of pump stators. An infrequent problem was the loss of pump capacity due to erosion of the rotor surface after what appeared to be a chrome plating failure. Typical operating life for a stator and rotor was 1000 and 2000 hours, respectively.

31.6 ALKALI ADDITION SYSTEMS

31.6.1 Lime

The slaked lime preparation system consisted of a pebble lime storage silo, a screw feeder, a Portec-Cahaba lime slaker, a slaked-lime holding tank and associated feed pumps. Fresh water was used to slake the lime to a slurry of approximately 20 weight percent solids. For the test period the system was operated with lime for only 6-1/4 months. The system provided fair reliability. Maintenance was limited to the replacement of the lime grit screen on nine occasions and the motor for the pebble lime screw feeder on two occasions.

31.6.2 Limestone

The limestone slurry preparation system consisted of a limestone drying/grinding system, four limestone bins, a weigh belt feeder, a limestone slurrying/surge tank, and associated feed pumps.

For slurrying purposes, pulverized limestone was belt-fed into the 400-gallon limestone slurry preparation tank. Slurry solids concentration was controlled at a nominal 60 weight percent.

Considering the system usage, the equipment provided acceptable performance with moderate maintenance. Most of the maintenance was associated with the drying/grinding system. The major maintenance activities were as follows:

- In April 1979, the 125-Hp classifier blower motor failed and was replaced.

- The limestone dryer burner control regularly malfunctioned and required maintenance. Optical sensors (fire eyes), relays, and the fire eye amplifier were replaced.

- In May 1979, portions of the limestone dryer refractory were repaired with Kaocrete B.

- In October 1979 the limestone classifier failed to perform. The resulting maintenance included:
    - Installing new bags in the limestone silo baghouse
    - Inspecting seals and balls in the ball mill
    - Lubricating the classifier fan motor bearings
    - Changing oil and cleaning both bearing journals on the ball mill
    - Installing air hose and nozzles to provide an air purge for the baghouse
    - Replacing the bucket elevator drive and motor sprockets
    - Checking the baghouse timer
    - Fabricating a screen for the classifier fan
    - Replacing the vanes on the rotary air block valve located on the baghouse hopper

31.7 INSTRUMENTS

31.7.1 In-line pH Meters

During the first part of this test period, process pH was measured using Uniloc Model 312L submersible electrode assemblies. These assemblies were manufactured by Universal Interloc, Inc.

Service requirements for the submersible assemblies consisted of periodic cleaning with a hydrochloric acid/water solution and buffering of the electrodes, generally every 2 or 3 days to ensure accuracy. On infrequent occasions, the electrode assembly failed for assorted reasons, such as wet electrical contacts, bad reference or sensing electrodes or off-gassing of the slurry. In an effort to eliminate the effects of slurry off-gassing and wet contacts, the venturi/ spray tower pH meters were modified in the field to a large volume flow-through pH meter (Figure 31-1). The modification was successful and was applied to the TCA pH meters in February 1979.

To ensure the accuracy of the process pH meters, a laboratory pH measurement of slurry which was sampled continuously from the system was made once every two hours for comparison purposes. This procedure enabled maintenance of pH control within ±0.2 pH units of the desired set point for conventional lime/limestone scrubbing and within ±0.1 pH units of the desired set point for adipic acid enhanced lime/limestone scrubbing.

A test process pH meter manufactured by Electrofacts was installed and tested in March 1979. After less than a week of operation the electronic circuitry failed and the tests were suspended. In November and December 1980, the meter was retested as part of a pH/stoichiometric control system developed by B. Harris of EPA and P. Garret of the University of Cincinnati (EPA Grant #R80575803). The Electrofacts electronics were not operable, and a modified Uniloc system was satisfactorily substituted.

31.7.2 SO_2 Analyzers

A Du Pont Model 400 UV split-beam photometer, equipped with an automatic zeroing and air purging system (1 minute every 10 minutes frequency), was used to measure SO_2 concentrations. Separate meters were located at the inlet and outlet of each scrubber. The instrument was accurate and reasonably trouble-free. Maintenance requirements were limited to cleaning the sample cell and sample lines approximately once every 1 or 2 months and to cleaning the particulate

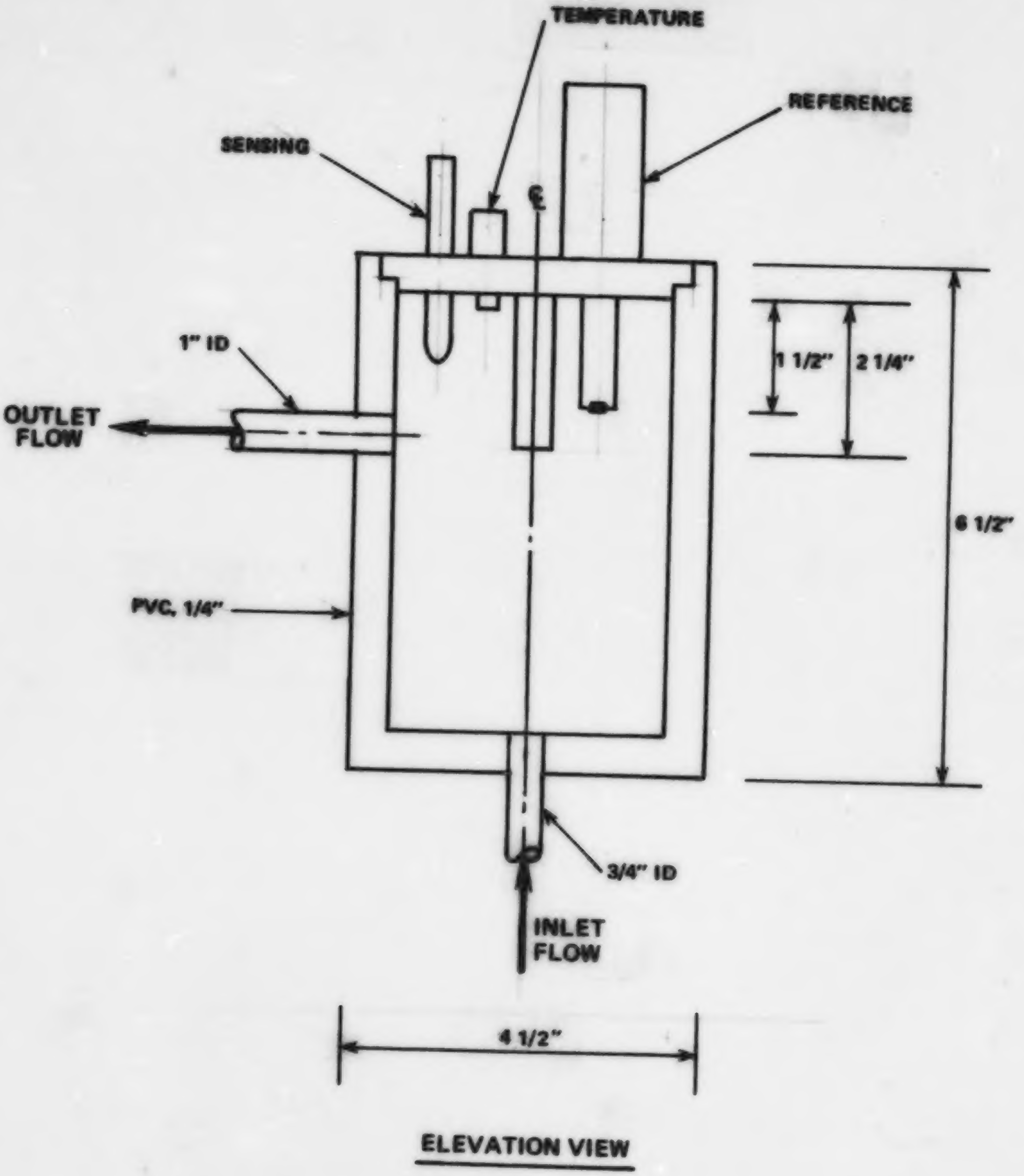

TEMPERATURE
REFERENCE
SENSING
℄
1" ID
OUTLET FLOW
1 1/2"
2 1/4"
6 1/2"
PVC, 1/4"
3/4" ID
INLET FLOW
4 1/2"
ELEVATION VIEW

Figure 31 - 1

Flow - through pH Meter Vessel Assembly

filter from once a day to once every 3 weeks. In September 1980 chronic plugging of the inlet sample lines with a dark black residue occurred. The residue was believed to be a vapor when it first entered the sample lines. The problem was resolved by the installation of a cold trap upstream of the existing Du Pont condensation trap (Figure 31-2). The trap operated at a temperature range of 80° to 86°F and effectively reduced line plugging. The trap was cleaned approximately once per week. Plugging by the black residue was not experienced in the venturi/spray tower outlet or in the TCA inlet and outlet. The use of the trap was discontinued after approximately 1-1/2 months because the residue ceased to be present.

Other maintenance on the four Du Pont meters included:

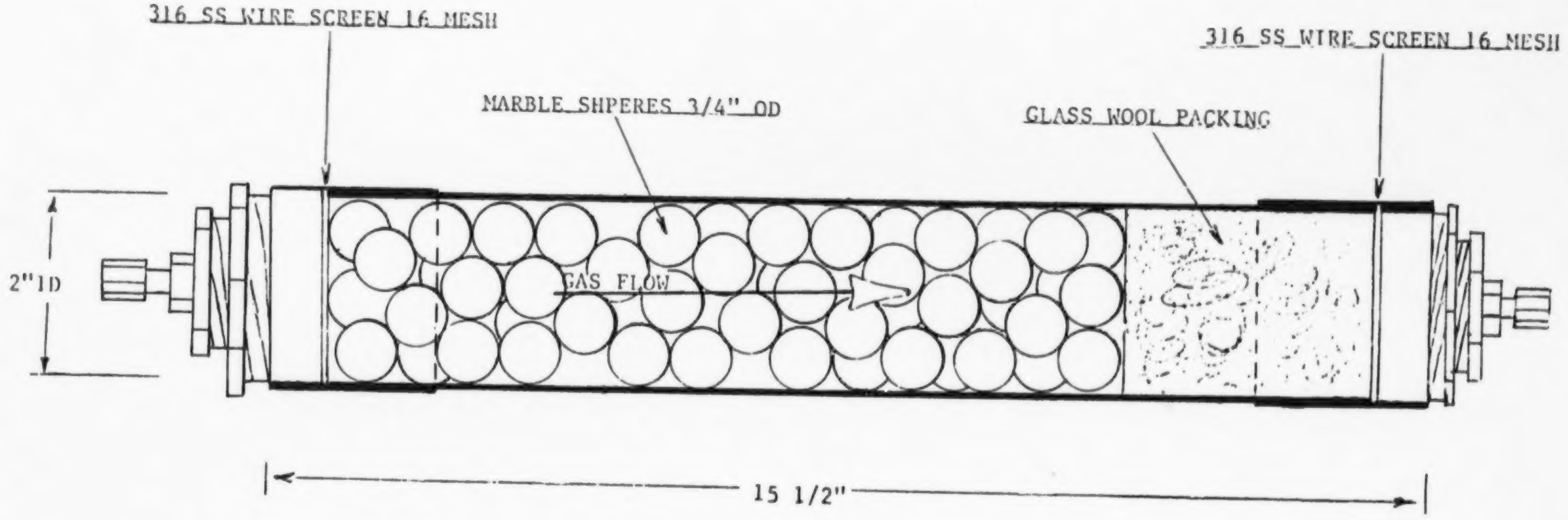
- Replacement of the ultraviolet lamp (16 times)
- New optical calibration filters installed in the spray tower system inlet analyzer on September 30, 1980
- New optics installed in the TCA inlet analyzer on October 9, 1980
- Repair of infrequent leaks at fittings
- The rebuilding of the venturi/spray tower inlet and outlet vacuum regulators on January 28, 1981 and December 2, 1980, respectively.

The calibration guidelines used at Shawnee are outlined in Table 31-3 .

31.7.3 In-Line O_2 Analyzer

Oxygen concentration in the inlet flue gas was initially measured with a Teledyne Model 9500 meter which was put in service in 1977. The meter used a micro-fuel cell as the sensing element. Operating experience during this period consisted of frequent unstable readings and fuel cell failure.

In November 1978 four Thermox WDG III O_2 analyzers were installed at the inlets and outlets of the venturi/spray tower and TCA. The analyzer element consisted


316 SS WIRE SCREEN 16 MESH
MARBLE SHPERES 3/4" OD
GLASS WOOL PACKING
316 SS WIRE SCREEN 16 MESH
GAS FLOW
2"ID
15 1/2"

1. Trap located downstream of heat-traced sample tubing and just upstream of the SO_2 analyzer moisture trap.
2. Materials of construction are 316 SS.

Figure 31-2

Condensation Trap To Eliminate Plugging on SO_2 Sample Lines

Table 31-3

SO_2 ANALYZER CALIBRATION AND VERIFICATION SCHEDULE

1. SO_2 analyzers were calibrated with optical filters 3 times per week (Monday, Wednesday, Friday).
2. SO_2 analyzers were calibrated with calibration gas once per week.
3. Once per month the following verification procedures were carried out on each SO_2 analyzer:
    - (a) The analyzers were calibrated with calibration gas.
    - (b) The flue gases were analyzed independently from the analyzer by EPA Method 6. Method 6 analyses were run in sets of 3 until the average of a set agreed with the analyzer within 10% or 30 ppm, whichever was greater.
4. SO_2 calibration gases were analyzed by Method 6 once monthly prior to Step 3 above.

NOTES:

(a) Calibration gas SO_2 concentrations were verified by Method 6. If the tag value agreed within 3% or 30 ppm (whichever was greater) of the average of three Method 6 analyses, the tag values were used. If it did not, three more Method 6 analyses were performed. If the second set of Method 6 analyses agreed with the first then the average of the two sets of Method 6 values was used.

(b) Calibration gases included synthetic air or nitrogen for instrument zeroing and SO_2 in nitrogen for instrument span adjustment.

of a high temperature electrochemical cell constructed of zirconium oxide. Initially the analyzers were installed to sample gas directly from the gas duct without sample gas conditioning (moisture and particulate removal). After approximately six months of service, the instruments at the scrubber inlets were judged to be accurate but unreliable due to the frequent sample line and aspirator pluggage. In July 1979, the analyzers on the scrubber inlets were relocated so as to be in tandem with the existing Du Pont analyzers. The Thermox analyzers sampled a slip-stream after the Du Pont purge air solenoid valves. The Thermox outlet gas was reintroduced into the Du Pont system prior to the Du Pont vacuum regulator. After the modification, the instruments operated with acceptable accuracy and reliability. Cleaning of the sample line was required approximately once per month per instrument.

The analyzers on the scrubber outlets were not relocated to the Du Pont analyzers as they did not experience the serious plugging problems that the inlet analyzers experienced. The outlet meters were cleaned approximately once every 3 or 4 weeks.

31.7.4 Magnetic Flowmeters

The Foxboro Series 1800 and 2800 magnetic flowmeters ranged in size from 1-1/2 to 8 inches in diameter. Service applications included process water, scrubber slurry, lime slurry and limestone slurry. Periodic scale removal by hydrochloric acid/water wash was required to maintain accuracy and sensitivity. Of the 19 meters in service, the total number of meter cleanings was forty-two. For the large meters, satisfactory meter accuracy was maintained by electrical purging once per shift with the Foxboro Magnetic Flow Meter Electrode Cleaning Assembly. The electrode cleaning assembly applied line power voltage between the transmitter electrodes and the transmitter tube. The current flow oxidized away electrode deposits and thus relieved the condition of high resistance between electrodes and the process liquid for normal accurate operations. The meters were considered reliable, acceptably accurate, and easily serviced.

31.7.5 Density Meters

Both Dynatrol Model 1 CL-10HY U-tube density meters and Ohmart radiation density meters were used at Shawnee, primarily for monitoring the density of the scrubber slurry and the makeup limestone slurry.

The U-tube density meters were preferred because the tubes could be serviced onsite and a radiation safety specialist was not required. In the field the preferred U-tube replacement material was Hastalloy C.

31.7.6 Level Measurement

During this program, Milltronics Miniranger Ultrasonic Level Systems replaced the Foxboro Differential Pressure Model 617FEM where accurate and reliable measurements of level were required. The first Milltronics was installed for testing in March 1979. Results were satisfactory and five more instruments were subsequently purchased and installed. The instruments were easily serviced and operated trouble-free except for one transducer failure. It should be noted that care should be taken during installation to insure that the scanning area of the element is free of obstacles.

Those tanks without Milltronics level indicators used the Foxboro differential pressure (atmosphere/tank pressure) Model 617FEM with a Teflon coated stainless steel diaphragm. The instrument had three recurring problems:

- Deposits of mud or scale on the diaphragm caused false readings. Cleaning of the diaphragm required draining of the tank.

- Changes in slurry density changed the indicated level.
- Transmitter electronics were sensitive to the ambient temperature. Foxboro claims that the problem has been corrected on newer models.

31.8 DEWATERING EQUIPMENT

31.8.1 Centrifuge

The machine used was a Bird 18 in. x 28 in. solid bowl continuous centrifuge which operated at 2050 rpm. The primary material of construction was 316L stainless steel with stellite hardfacing on the feed ports and solids discharge ports. The bowl head plows and case plows were replaceable. The pool depth was set at 1-1/2 inches. No cake washing was performed in this machine. Two conveyors, one with tungsten carbide hardfacing and one with ceramic hardfacing, were tested. The tungsten carbide conveyor was installed on November 20, 1978, and removed on June 3, 1979, after approximately 3750 hours of operation. The conveyor exhibited minor wear and the reason for the removal was to test the ceramic conveyor. The ceramic conveyor was operated for approximately 6210 hours from June 29, 1979, to July 22, 1980. Upon inspection, the conveyor showed minor wear with some evidence of chipping of the ceramic. Generally the machine was judged to operate satisfactorily as a sludge dewatering service but showed serious erosion at the solid discharge bowl head and plows.

31.8.2 Vacuum Drum Filter

An Ametek 3 ft x 6 ft vacuum drum filter without cake wash was operated at the facility for waste sludge dewatering. Cake discharge was achieved by a snap-blowback cycle.

As had occurred in earlier programs at Shawnee, filter cloth blinding continued at an unusually high rate. Typical cloth life was less than 600 hours. The cloths used were Ametek Olefin (STE-F9D8-HJO) and Lamports Polypropylene (7512-SHS). No noticeable differences in performance were observed between the two cloths.

31.8.3 Horizontal Belt Vacuum Filter

A 4 x 20 ft horizontal belt vacuum filter manufactured by Straightline Filters was installed at the facility in late 1979. The machine had 70 ft^2 active filter area and was constructed of 304 SS. The cloth was a SPP-10 (51 inches x 53 ft 4 inches), and the belt was neoprene. The filter was originally used for 6 months during the DOWA process testing by TVA.

The filter operated effectively as a dewatering device yielding moisture content consistently lower than that obtained on the drum filter and centrifuge. Periodic maintenance consisted of repairing the separation of the filter cloth from the elastomer belt, patching the cloth, replacing the cloth/belt unit, and adjusting the alignment or tension on the belt. The tendency for cloth blinding was noticeably less than what was experienced with the drum filter. Since December 1979, only three cloths were replaced.

31.9 OTHER MATERIALS AND EQUIPMENT

During the reporting period the following equipment and materials were monitored:

- Lining and piping
- Control valves
- Strainers

31.9.1 Lining and Coatings

Lining and/or coating materials for equipment at the Shawnee Test Facility generally consisted of neoprene (for the pipes, pumps, scrubber internal walls and small tanks) or Flakeline 103 (for the large effluent hold tanks and clarifiers). Flakeline 103 is a bisphenol-A polyester resin filled 25 to 35 percent with glass flake and was manufactured by the Ceilcote Company.

Both neoprene lining and Flakeline coating showed a continued low rate of erosion and other deterioration. Delamination of rubber occurred at six isolated areas each of less than one square foot, principally in the venturi/ spray tower.

Whenever necessary, successful patch repairs were made using Epoxylite-203 (Epoxylite Corp., Anaheim, California), an epoxy resin formulated with selected fillers. One failure of epoxylite occurred in the venturi/spray tower, but the cause was believed to have been insufficient cure time during the previous repair attempt. The resin was used with Epoxylite No. 301 amine hardener.

The D-208 oxidation tank was inspected January 15, 1980, in preparation for its use on the venturi/spray tower. The materials of construction were carbon steel with a polyester coating. The coating had failed over most of the tank surface, showing blistered areas caused by the penetration of corrosives. In February, the tank was sand blasted and coated with 3 coats of Ceilcote Flakeline No. 252 primer. In October 1980 the coating was inspected and was observed to have failed on a few baffle edges that the primer application missed. Epoxylite 203 was used to patch these areas. In March 1981, the tank was inspected and the coating was in good condition.

31.9.2 Piping

After 7-1/2 years in service, blisters that were last reported 2-1/2 years ago were still present in some sections of the neoprene lined pipe. The number of blisters did not appear to have increased and did not cause pipe failures or blockages.

Schedule 80 PVC 1120 (ASTM D-1785) pipes of 6 and 8-inch diameter were in service at locations in the TCA and venturi/spray tower recirculating slurry lines. Operation with PVC piping was satisfactory with respect to corrosion and erosion over the last three years. During the winter some out-of-service lines that were improperly drained cracked due to freezing.

Due to time and cost restraints, approximately 50 feet of 16-inch diameter carbon steel pipe (unlined) was installed in the scrubber effluent return to D-208 tank and the slurry cross-over from D-208 to D-101 tanks. The pipe was installed in February and March 1980, and did not develop leaks.

31.9.3 Valves

The use of valves was minimized in recent years. Most slurry flows are controlled by variable speed pumps. Those valves that were used in intermittent slurry service with success were Garlock high density polyethylene valves (Gar-Seal 300 Series UHMPE, 2-inch butterfly) and Keystone rubber coated valves (Model 99, Waffle Style, C1 Body-EPDM Model Disk with protective cover over 316 SS EPDM seat).

31.9.4 Strainers

Slurry strainers were used to reduce the plugging of slurry nozzles with debris and other foreign material. Applications included slurry to the presaturators, spray tower, TCA, and venturi.

The strainer types were Elliott and Hayward (Table 31-4) and neither type was shown to be particularly better than the other. The sizes ranged from 2-inch Y strainers to 8-inch basket strainers. For the larger strainers, carbon steel was used because more exotic materials were too costly for the facility's needs.

Two Hayward strainers in the main recirculation line of the TCA were lined with

Table 31-4

STRAINER INVENTORY

Quantity	Type/Model	Location/Service	Size	Remarks
1	Hayward	G204	6", #50	C.S./S.S. Dual Basket
1	Hayward	G104	6", #50	C.S./S.S. Dual Basket
1	Hayward	G201	8", #50	C.S./S.S. Dual Basket
3	Meuller NC	S.T. Presaturator	2", 1616W	316 SS
1	Meuller NC	TCA Presaturator	2", 1616W	316 SS
2	Paget-C	TCA Presaturator	SC3-103A	316 SS
1	Elliott	G101	6"	C.S./S.S. Dual Basket Installed 1974; Removed 1979

Ceilcote No. 103 glass-filled epoxy in October 1979. No measured improvement in erosion/corrosion resistance has yet been observed when compared to carbon steel strainers.

Strainers were judged to be effective in removing debris when properly maintained. Maintenance consisted of :

- Replacing the eroded basket
- Refilling eroded areas on the basket support edge with welding rod
- Refilling corrosion holes in the strainer casing near the discharge throat with welding rod

31.9.5 Materials Testing

During this test period, TVA studied the effects of adipic acid enhanced limestone scrubbing on materials of construction.

Field Testing. On July 19 and 20, 1978, corrosion test coupon racks were installed in the TCA and venturi/spray tower trains. Each rack had 1 rubber and 14 metal specimens. The coupon racks were installed at locations 2005 (inside the TCA) and 2008 (tank D-204) in the TCA train and at locations 1005 (inside the spray tower) and 1008 (EHT D-101) in the venturi/spray tower train. The composition of each coupon was as follows:

1. AL6X (stainless steel)
2. Carpenter 7-Mo
3. Carpenter 20 Cb-3
4. Cor-Ten A
5. Hastelloy C-276
6. Hastelloy G
7. Incoloy 825
8. Inconel 625
9. Jessop 700
10. Mild steel A-283
11. Nitronic 50
12. Type 216 SS
13. Type 316L SS with 2.6 % Mo
14. Type 317L SS with 3.2 % Mo
15. Neoprene

Table 31-5 gives information pertinent to test conditions, lists the materials tested, and gives the results of these tests. For the stainless steels and highly alloyed materials, the corrosion rates were negligible or less than one mil per year with only minute localized attack, if any. Mild steel and Cor-Ten A were attacked at rates that ranged from 1 to 150 mils per year with maximum pitting 10 mils deep. The least corrosion occurred in the effluent hold tanks, 1 to 2 mils per year. The greatest corrosion, 140 and 150 mils per year, occurred at test location 1005 below the mist eliminator in the venturi/spray tower system. These rates are within the range of those for the five previous series of corrosion tests conducted at the same locations before the use of adipic acid was begun (References 1, 3, 4, and 5). Neoprene was in good condition for all test locations.

On October 8, 1978, an additional rack of corrosion test coupons was installed in the trap-out tray of the spray tower to evaluate the effects of low pH scrubber slurry containing adipic acid on plastics and rubbers. The composition of the rack was:

- Natural rubber
- Neoprene
- Hypalon
- Thermal plastic rubber
- Mild steel A-283
- Nitrile foam
- Butyl 1580
- FRP, Bonstrand 4000
- PVC, Lucoflex
- Polypropylene
- Polyethylene type 1
- Viton

Table 31-6 shows the materials tested, changes in the specimens during the 104-day exposure period, and their evaluation. The greatest changes in weight for the nonmetallic materials were an increase of 6.6 percent for Viton and a loss of 3.1 percent for the nitrile foam sphere; these two materials also showed the

Table 31-5

CORROSION TESTS CONDUCTED AT THE SHAWNEE TEST FACILITY DURING ADIPIC ACID TESTING

Scrubber system	Venturi/Spray Tower		TCA	
Test period	7/20/78 to 2/3/79		7/19/78 to 11/2/78	
Operating days (hours)	169.4 (4065)		96.3 (2312)	
Idle days (hours)	28.6 (686)		9.7 (232)	
Test media	Gas and liquor	Effluent liquor	Gas and droplets	Effluent Liquor
pH range	4.5-8.0	4.7-6.3	4.6-7.3	4.3-5.4
Adipic acid content, ppm	1380-1615	1380-1615	350-1620	350-1620
Test location	1005	1008	2005	2008
Corrosion rate of metals, mils/yr[a]				
AL6X, weld AL6X	Neg.	<1	Neg.	Neg.
Carpenter 7-Mo, weld 316L	<1, pair	<1	<1, C7	Neg.
Carpenter 20 Cb-3, weld Carpenter 20 Cb-3	<1	Neg.	Neg.	Neg.
Cor-Ten A, weld E8018	150	1, Pm	28, P10	1, P2
Hastelloy C-276, weld Hastelloy C-276	<1	Neg.	Neg.	Neg.
Hastelloy G, weld Hastelloy G	<1	Neg.	Neg.	Neg.
Incoloy 825, weld Incoloy 65	<1	Neg.	Neg.	Neg.
Inconel 625, weld Inconel 625	<1	Neg.	Neg.	Neg.
Jessop 700, weld Comete S2	<1	Neg.	Neg.	Neg.
Mild steel A 283, weld E6012	140	2, P3	28, P8	1, P2
Nitronic 50, weld Nitronic 50	<1, Cm	Neg.	Neg., Cm	Neg.
Type 216, weld Type 216	<1, Cm	Neg.	Neg.	Neg.
Type 316L (2.6% Mo), weld Type 316L	<1, Cm	Neg.	Neg.	Neg.
Type 317L (3.2% Mo), weld Type 309C6	<1, C7	Neg.	<1	Neg.
Evaluation of elastomer				
Neoprene	Good	Good	Good	Good

(a) Neg. = corrosion rate was negligible, P = pit, and C = crevice to the depth in mils shown by number; m = minute pit or crevice.

Table 31-6

RESULTS OF CORROSION TESTING OF ELASTOMERS, RIGID PLASTICS, AND MILD STEEL IN THE SPRAY TOWER WITH LIMESTONE SLURRY CONTAINING ADIPIC ACID

Scrubber system	Venturi/spray tower
Test period	10/8/78 to 2/3/79
Operating days (hours)	104.3 (2503)
Idle days (hours)	13.7 (329)
Runs	907-1A through 908-1A
Test medium	Gas and liquor
pH range	4.9-5.7
Test location	Trapout tray (1018)

Test specimen		Change[a] in specimen during the 104-day test period			
Material	Configuration	Hardness, durometer (Shore "A2")[b]	Diameter, %	Weight, %	Evaluation[c]
Elastomers					
Butyl 1580	2-inch disk	-2	+0.9	+0.9	Good
Hypalon	2-inch disk	0	-1.0	-1.6	Good
Natural rubber	2-inch disk	+1	-0.5	-0.4	Good
Neoprene	2-inch disk	0	-0.8	-0.8	Good
Nitrile foam	1.8-inch sphere	(d)	-5.2	-3.1	Poor(e)
Thermoplastic rubber	1.5-inch sphere	(d)	+1.7	+1.9	Good
Viton	2-inch disk	+3	+6.2	+6.6	Poor(e)
Rigid plastics					
Bondstrand 4000 (epoxy)	2-inch disk	--	0	+0.1	Good
Polyethylene Type I	2-inch disk	--	0	+0.6	Good
Polypropylene	2-inch disk	--	-0.1	+0.2	Good
Polyvinyl chloride	2-inch disk	--	0	-0.4	Good
Metal					Corrosion rate, mils/yr
Mild steel, A283	2-inch disk	--	--	--	>225(f)

(a) An increase in value is preceded by "+"; a decrease in value is preceded by "-".
(b) Instrument not calibrated for testing hard materials.
(c) Resistance to chemical attack as well as to change in the physical properties was considered in the evaluation.
(d) Could not determine hardness due to configuration of specimen.
(e) Chemical attack of specimen.
(f) Specimen failed before the test period ended.

greatest changes in diameter, an increase of 6.2 percent for Viton and a loss of 5.2 percent for the nitrile foam sphere. Little or no changes in hardness occurred to the elastomers. All the rigid plastics were in good condition after the test. Of the elastomers tested, Butyl 1580, Hypalon, natural rubber, neoprene, and thermal plastic rubber (sphere) were in good condition, whereas nitrile foam (sphere) and Viton were in poor condition; these specimens had been attacked chemically. Mild steel A 283, failed during the test with a corrosion rate greater than 225 mils per year. The corrosion data for mild steel showed that exposure conditions at the trapout tray were more severe than those at either test location shown in Table 31-5.

On March 7, 1980, corrosion test coupon racks were installed in the top of the spray tower (test location and spool number 1005), in the bottom of the spray tower (test location and spool number 1006), in D-101 tank (test location number 1008), and in the D-208 tank (test location number 1019, on spool number 2013). The spool in the D-208 tank was initially installed on the oxidation air sparger at the bottom of the tank below the bottom set of agitator blades. When loss of pump suction required relocation of the air sparger on March 12, the spool was moved to a location immediately above the bottom set of agitator blades.

The specimens were removed from the system May 28, 1980.

Table 31-7 gives information pertinent to test conditions, exposure periods, corrosion rates for metals, and the condition of neoprene after the test. The operating time was not the same for all units of equipment. Tanks sometimes remained filled with slurry that was agitated while other units were idle.

All alloys tested showed good resistance to corrosion, one mil per year or less, on the basis of weight loss at each of the four test locations except for Cor-

Table 31-7

RESULTS OF CORROSION TESTS CONDUCTED ON THE VENTURI/SPRAY TOWER SYSTEM WITH LIMESTONE SLURRY CONTAINING ADIPIC ACID

Corrosion specimens				
Exposed in	Gas and liquor	Gas and liquor	Liquor	Liquor
Test location, No.	1005	1006	1008	1019
Exposure period	3/7/80-5/28/80	3/7/80-5/28/80	3/7/80-5/28/80	3/7/80-5/28/80
Operating time, hr (days)	1523 (63.5)	1523 (63.5)	1900 (79)	1850 (77)
Idle time, hr (days)	445 (18.5)	445 (18.5)	68 (3)	118 (5)
Exposure conditions				
Gas				
Temperature, °F	125-130	125-130	--	--
Velocity, ft/sec	5.4-9.4	5.4-9.4	--	--
Flow rate, acf/m at 300°F	20,000-35,000	20,000-35,000	--	
Air flow in forced oxidation, acf/m	--	--	--	90-300
Inlet gas composition, volume %				
SO_2	0.1-0.3	0.1-0.3	--	--
CO_2 (estimated)	10-18	10-18	--	--
O_2	3.2-5.6	3.2-5.6	--	--
H_2O (estimated)	8-15	8-15	--	--
HCl (estimated)	0.01	0.01	--	--
N_2 (estimated)	74	74	--	--
Fly ash, gr/scf	3-5	3-5	--	--
Liquor				
Temperature, °F	125	130	90-130	90-120
Solids, undissolved, % by wt	--	--	13.5-17.1	13.5-17.1
Solids, dissolved, % by wt	--	--	1.2	2.3
pH	--	--	4.2-5.4	4.2-5.4
Adipic acid, ppm	--	--	1190-4850	1190-4850
Ionic composition, ppm				
$SO_3^=$	--	--	763 (210-1300)	763 (210-1300)
$SO_4^=$	--	--	1806 (1610-2115)	1806 (1610-2115)
Ca^{++}	--	--	4126 (3450-5500)	4126 (3450-5500)
Mg^{++}	--	--	827 (700-1075)	827 (700-1075)
Na^+	--	--	148 (110-195)	148 (110-195)
K^+	--	--	129 (100-190)	129 (110-190)
Cl^-	--	--	6761 (5485-8900)	6761 (5485-8900)
Corrosion rate of metals, mils/yr[(a)]				
AL 6X, weld AL 6X	Neg.	<1	Cm	Neg.
Carpenter 7-Mo, weld 316L	<1, Cm	1, C5	<1, C1	<1
Carpenter 20Cb-3, weld Carpenter 20Cb-3	<1, C1	<1, C4	Neg.	Neg.
Cor-Ten A, weld E8018	83, C36	276, C75	16, P6	27
Hastelloy C-276, weld hastelloy C-276	<1	<1	Neg.	Neg.
Hastelloy G, weld Hastelloy G	<1	<1	Neg.	Neg.
Incoloy 825, weld Incoloy 65	<1	<1	Cm	Neg.
Inconel 625, weld Inconel 625	<1	<1	Neg.	Neg.
Jessop 700, weld Comete S2	<1	<1, C5	Cm	<1
Mild steel A 283, weld E6012	84	402	27, P6	37
Nitronic 50, weld Nitronic 50	<1, Cm	<1	Neg.	Neg.
Type 216, weld Type 216	<1, Cm	<1	Neg.	Neg.
Type 316L, weld Type 316L	<1, C2	1, C2	<1, Cm	Neg.
Type 317L, weld Type 309Cb	<1, C1	1, C3	Neg.	Neg.
Evaluation of rubber[(b)]				
Neoprene	Good	Fair	Good	Good

(a) Negligible (Neg.) indicates corrosion rates of less than 0.05 mil per year; <1 indicates corrosion rates of 0.05 to 0.49 per year; "C" or "P" preceding a number indicates crevice corrosion or pits, respectively, during the exposure period to depth in mils shown by the number; and "Cm" or "Pm" indicates minute crevice or minute pit.

(b) Evaluation: Good, little, or no change in condition of specimen; Fair, definite change probably could be used.

Ten A and mild steel A 283. The corrosion rates in mils per year for these two alloys were 16 to 276 for Cor-Ten A and 27 to 402 for mild steel A 283. Crevice corrosion (minute to 5 mils deep) occurred on some of the other alloys. Localized attack did not occur on specimens of Hastelloy C-276, Hastelloy G, and Inconel 625. The comparative severity of environments at the four test locations used in this series of tests is indicated by the results for Cor-Ten A and mild steel A 283. The test locations are listed by number in the order of increasing severity--1008, 1019, 1005, and 1006.

Test locations 1005 and 1008 were used in both the first and the second series of corrosion tests (Tables 31-5 and 31-7, respectively). Table 31-8 gives a limited comparison of conditions at these test locations and gives the corrosion rates for Cor-Ten A and mild steel A 283 in both series of tests. These data show that the higher adipic acid content and the lower pH range in the second series gave lower corrosion rates at test location 1005 (below the mist eliminator) and higher rates at test location 1008 (in the effluent hold tank) than occurred at these locations in the first series of tests. It is doubtful that the difference (30 scfm average) in the air flow rate used for forced oxidation in the two series would account for the change in trend of corrosion rates of Cor-Ten A and mild steel A 283.

Because there was a simultaneous change in the range of slurry pH, in adipic acid content, and in the mode of operation (second series with single-loop, two-tank mode), it is not obvious whether only one or all three of these changes were factors causing the difference in corrosion rates of Cor-Ten A and mild steel A 283 in the first and second series of tests; however, there was no appreciable difference in corrosion resistance of the other alloys tested in both series; all rates were one mil per year or less with moderate localized attack of some alloys.

Table 31-8

COMPARISON OF EXPOSURE CONDITIONS AND CORROSION RATES
FOR TWO SERIES OF TESTS ON THE VENTURI/SPRAY TOWER SYSTEM

Test series	Second[(a)]		First	
Test location	1005	1008	1005	1008
Test Conditions				
pH range	4.2-5.4	4.45-5.00	4.5-8	4.7-6.3
Air for oxidation, SCFM[(b)]	210 (90-300)	210 (90-300)	240 (130-260)	240 (130-260)
Adipic acid, ppm	1190-4850	1190-4850	1380-1615	1380-1615
Corrosion rate, mils/yr				
Cor-Ten A	83	16	150	1
Mild steel A 283	84	27	140	2

(a) Operation was the single-loop, two-tank mode
(b) Values are the average for the steady-state operating period (range)

In November 1978 a test coupon constructed of 316 stainless steel and covered with an approximately 1/4 inch thick layer of Metalife Ceramic Steel U. S. (Utility System) 401 was placed on the east venturi plug support guide vane for evaluation in a flue gas/slurry atmosphere, a location of severe abrasive service. The shield was removed on December 6 after approximately 428 hours of exposure. Significant portions of the coating were eroded, exposing bare metal. Additionally, some erosion was evident in the 316 stainless steel substrate.

Laboratory Testing. Tests were made of seven elastomers, four rigid plastics, and mild steel A 283, in a solution containing a nominal 5000 ppm of adipic acid in distilled water for 56 days at 140°F. The pH of the solution was 3.0. One specimen of each material was tested separately immersed in 1.5 liters of solution contained in a 1/2 gallon jar which was heated in a water bath with automatic temperature control. A similar test was also made of a nitrile foam sphere in a nominal 1600 ppm adipic acid solution that contained 10 percent by weight of calcium sulfite. The pH of the solution was 7.4. The solutions were agitated by shaking the jars mildly twice per day on work days. New solution was used each week in the test of mild steel; the solutions in all other tests were used throughout the 56-day exposure period.

Table 31-9 lists the materials tested, the configuration of test specimens, the evaluation of the nonmetallic materials and the corrosion rate of mild steel, and gives changes that occurred in solutions and specimens during the exposure period.

The adipic acid content was determined for six of the test solutions after completion of the tests. The solution that contained natural rubber showed no loss of adipic acid. The five other solutions showed a loss (from the original 4962 ppm) of adipic acid during the test. Listed in the order of increasing

Table 31-9

LABORATORY TESTS OF ELASTOMERS, RIGID PLASTICS, AND MILD STEEL IN SOLUTIONS[a] OF ADIPIC ACID AT 140°F FOR PERIODS OF 56 DAYS

Test specimen		Test Solution after 56 days[c]		Changes[b] in specimens during the 56-day test period: Strip				Sphere		
Material	Configuration	Adipic acid, ppm	pH	Hardness, durometer (Shore "A2")	Tensile strength, %	Elongation, %	Weight, %	Diameter, %	Weight, %	Evaluation[d]
Solution containing 4962 ppm adipic acid, pH 3.0										
Elastomers										
Butyl 1580	1-1/4 x 5-inch strip	--	3.1	-1	+8.6	+15	+0.7	--	--	Good
Hypalon	1-1/4 x 5-inch strip	4855	3.0	-1	+1.3	-9	+0.2	--	--	Good
Natural rubber	1-1/4 x 5-inch strip	4966	3.1	0	+36.9	+4	+3.7	--	--	Good
Neoprene	1-1/4 x 5-inch strip	4631	3.3	-3	-18.0	-17	+15.3	--	--	Fair
Viton	1-1/8 x 5-inch strip	--	3.5	+20	-3.6	-15	+3.7	--	--	Fair
Nitrile foam	1.9-inch diam. sphere	4073	3.4	--	--	--	--	+9.8	+267.5	Poor[e]
Thermoplastic rubber	1.5-inch diam. sphere	--	3.1	--	--	--	--	+1.2	+0.5	Fair[f]
Rigid plastics										
Bondstrand 4000	2-inch disk	--	3.1	--	--	--	+0.6	--	--	Good
Polyethylene Type I	1-1/4 x 5-inch strip	--	3.0	--	--	--	0	--	--	Good
Polypropylene	1-1/4 x 5-inch strip	--	3.0	--	--	--	0	--	--	Good
Polyvinyl chloride	1-1/4 x 5-inch strip	--	3.1	--	--	--	+0.3	--	--	Good
Metal										
Mild steel, A283	2-inch disk	2460[c]	5.1[c]	--	--	--	--	--	--	Corrosion rate, 138 mils/yr
Solution containing 1587 ppm adipic acid and 10% by weight of $CaSO_3$, pH 7.4										
Elastomer										
Nitrile foam	1.9-inch diam. sphere	<50	7.8	--	--	--	--	-12.0	+4.3	Fair[g]

(a) Distilled water was used to prepare solutions; each test specimen was immersed in 1.5 liters of solution.
(b) An increase in value is preceded by "+"; a decrease in value is preceded by "-"; only one specimen tested of each material.
(c) In the test of mild steel new solution was used each week; in all other tests the solution was used 56 days.
(d) Resistance to chemical attack as well as to change in the physical properties was considered in the evaluation.
(e) Chemical attack of specimen.
(f) Specimen was dimpled reducing its volume.
(g) Decrease in diameter of specimen; little chemical attack if any.

loss were the solutions that contained Hypalon, neoprene, nitrile foam, and mild steel A 283. Approximately 18 percent of the adipic acid was removed from the solution in the test of nitrile foam in 56 days. Apparently 50 percent of the adipic acid was consumed in corrosion of mild steel in one week (new solution used each week) that resulted in a corrosion rate of 138 mils per year.

After the 56-day exposure period the pH value of solutions used in the test of Hypalon, polyethylene Type I, and polypropylene had not changed from the original value of 3.0. The pH of solutions used in the test of other nonmetallic materials ranged from 3.1 to 3.5; that for nitrile foam sphere was 3.4 and that for Viton 3.5. The greatest change was in the solution (after one week) used for testing mild steel; the pH was 5.1.

When applicable, tests were made (one specimen only) of the nonmetallic materials to show any change in hardness, tensile strength, elongation, weight, and diameter. Hardness, strength, and elongation properties were not determined for the spheres and for the rigid plastics. No change was detected in the hardness of natural rubber during the test in nominal 5000 ppm adipic acid; three of the elastomers decreased one to three units on the durometer A hardness scale and Viton increased 20 units. The effect on tensile strength ranged from an 18 percent loss for neoprene to a 36.9 percent gain for natural rubber. A loss of elongation occurred to neoprene, Viton, and Hypalon while natural rubber and Butyl 1580 showed an increase. Seven of the nonmetallic materials showed low (0 to 0.7 percent) increases in weight, natural rubber and Viton increased 3.7 percent, and nitrile foam (sphere) increased 267 percent in weight even though chemical attack occurred. The materials tested are evaluated as follows:

Good resistance--Butyl 1580, Hypalon, natural rubber, Bondstrand 4000, polyethylene Type I, polypropylene, and polyvinyl chloride

Fair resistance--neoprene, Viton, and thermoplastic rubber

Poor resistance--nitrile foam

The corrosion rate for mild steel was excessive, 138 mils per year.

The test of a nitrile foam sphere in a solution containing nominal 1600 ppm adipic acid and 10 percent by weight of calcium sulfite (solution pH 7.4) at 140°F for 56 days showed a 12 percent decrease in the diameter of the sphere, 4.3 percent weight increase, and very little if any visible evidence of chemical attack. The adipic acid content of the solution had been reduced to less than 50 ppm and the pH had increased from 7.4 to 7.8. Because the sphere was considerably smaller in volume after the test, its resistance to deterioration under these conditions was rated "fair".

Section 32

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